EFFICIENCY AND DURABILITY OF WEARABLE SMART MATERIALS AND STRUCTURES

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PHD 2018

EFFICIENCY AND DURABILITY OF WEARABLE SMART MATERIALS AND STRUCTURES

BY

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THIS THESIS IS SUBMITTED TO THE UNIVERSITY OF BOLTON

IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR OF THE

DEGREE OF DOCTOR OF PHILOSOPHY

COLLABORATING ESTABLISHMENT:

PIRAEUS UNIVERSITY OF APPLIED SCIENCES

JANUARY 2018

DECLARATION

I, hereby, declare that the thesis is based on my original work except for standard definitions, quotations and citations which have been duly acknowledged, I also declare that it has not been previously or concurrently submitted for any other degree at any stage of learning or other institutions.

Contribution of co-authors

The following people are acknowledged as co-authors of the papers published as a requirement for the PhD program.

- Professor Elias Siores, PhD supervisor at Bolton University
- Professor Savvas Vassiliadis, PhD supervisor at Piraeus University of Applied Sciences
- Professor Derman Vatansever Bayramol at Namik Kemal University, Turkey. Professor Vatansever was involved in the production of the piezoelectric fibres at Bolton University.
- Dr Navneet Soin, post-doctoral research fellow at Bolton University. Dr Soin, offered guidance on polymer material analysis, mainly HPLC, FTIR and DSC measurements and carried out the measurements at Bolton University.
- Professor Kleanthis Prekas at Piraeus University of Applied Sciences. Professor Prekas offered guidance on reduction of noise in electronic systems.

- Professor Stylianos Mitilineos at Piraeus University of Applied Sciences. Professor Mitilineos offered guidance on the measurement of capacitance of materials.
- Professor Nikolaos Stathopoulos at Piraeus University of Applied Sciences. Professor Stathopoulos offered guidance on the properties of capacitive materials.

DEDICATION

for them that come after.

“Illegitimi non carborundum”

ABSTRACT

Piezoelectric polymer materials have been under investigation since the 1970's starting with the discovery of the piezoelectric effect in PVDF films by Kawai. Since then the piezoelectric effect has been detected among other polymers in polyureas, polyamides, and polypropylene and their copolymers. While the investigation of the piezoelectric effect was largely carried out on the film form of the polymers since 2010 interest has developed into the production methods, properties and applicability of melt spun piezoelectric textile fibres made of these polymers. The application of piezoelectric fibres could have a significant impact in wearable textiles as sensors, actuators, or energy harvesting modules. Current research is mostly centred onto production methods and fibre crystallinity characterization.

The research carried out in this PhD by publication project is concerned with piezoelectric textile fibres as electrically active elements. As such the research focused on the electrical behaviour of the fibres. The work carried out was three-fold.

Specifically, wearable textile materials undergo cleaning/ care treatments that are intrinsic to their function as wearables. These treatments may include washing, dry cleaning or sponging. Washing (cleaning treatment in a solution mainly containing water and an appropriate detergent at an elevated temperature or room temperature) is a common cleaning method. The effects of washing cycles on melt spun piezoelectric fibres remain under-investigated. For the first part of the research, piezoelectric melt spun fibres (PVDF, PP and PA-11) with two different cross sections (circular and rectangular), were mechanically stimulated by a rotating fin that impacted the fibres periodically. The resulting $V_{p\text{-}p}$ (peek to peek voltage), was measured on the original fibres and on the fibres following one wash cycle (adapted BS EN ISO 105-C06), using an oscilloscope. Based on the

results of this part of the research it was shown that the washing cycle effected the voltage response of the fibres depending on the fibre cross section and the fibre composition. The results of the research were presented in a paper titled “Investigation of the durability and stability of piezoelectric textile fibres” published in the Journal of Intelligent Materials Systems and Structures.

For the second part of the research, it was noted that according to the existing literature the research approach for the determination of the electrical response of the fibres utilized exclusively the measurement of the voltage produced by mechanical excitation of the fibres, in open circuit conditions. This approach is not sufficient to satisfactorily characterise the electrical behaviour of the fibres as power generating elements. By contrast, a sufficient measurement is the power production of the fibres as this also includes a measurement of the current produced. In order to supply these measurements a testing apparatus/ methodology was developed. The apparatus consists of a measuring station where the voltage and current produced are measured, and a means for periodic mechanical stimulation of the specimens. The equipment was used to determine the power generated by piezoelectric melt spun fibres (PVDF, PP and PA-11) with two different cross sections (circular and rectangular). The results of the research were presented in a paper titled “On the Measurement of the Electrical Power Produced by Melt Spun Piezoelectric Textile Fibres” published in the Journal of Electronic Materials.

Finally, considering the underlying premise of integration of fully textile based electronic components into textile substrates (e.g. wearable applications), 3D knitted fabrics that incorporated piezoelectric melt spun fibres were investigated with regards to their capacitive behaviour. Four different fabric structures were examined (different composition of the outside layers and different thickness). The capacitive behaviour of the samples was modelled based on the specific structural characteristics of the fabrics and the actual properties were determined using an Impedance Analyzer. Based on the results it was found that the theoretical model for the calculation of the capacitance of the samples appeared to be an acceptable approximation for the behaviour of the fabrics. Also, the ability to customise the required capacitance to suit the applications by specifying the dimensions of the 3D fabric and/or the density, the thickness or even the material of the interlaced fibres has also been shown to be possible.

Moreover, reviewing the results of a resonance test for a purely textile based parallel LC circuit, it was shown that it is possible to implement resonant circuits that are convenient for basic electronic applications (i.e. oscillators, filters, etc.). The results of the research were presented in a paper titled “Three-dimensional weft-knitted textile fabrics-based capacitors” published in the Journal of the Textile Institute.

This research project touched on some of the less thoroughly investigated research areas connected to the efficiency and durability of piezoelectric melt spun fibres and structures, with innovative results such as the development/ construction of the equipment that can be used for the measurement of the power produced by piezoelectric textile fibres as well as the investigation of the capacitive behaviour of the 3D knitted fabrics incorporating piezoelectric textile fibres and the conclusion that resonance is possible to achieve in a purely textile LC parallel circuit.

ACKNOWLEDGMENTS

I would sincerely like to thank my supervisors; Bolton University's Director of Research and Innovation, Professor Elias Siores, and Professor Savvas Vassiliadis and Professor Maria Raggoussi from the Piraeus University of Applied Science for their support and guidance throughout the research programme.

I would like to especially acknowledge the continued guidance of Professor Vassiliadis ever since our first encounter during my BSc years at the Piraeus University of Applied Sciences. From that point on, he has been an invaluable support and mentor in more than academic life and I consider myself immensely blessed to have met him.

I would be remiss if I did not mention the gracious support and help offered by the staff at the Piraeus University of Applied Sciences, New York College, and Bolton University.

Vincent Van Gogh said that “Close friends are truly life's treasures. Sometimes they know us better than we know ourselves. With gentle honesty, they are there to guide and support us, to share our laughter and our tears. Their presence reminds us that we are never really alone.” Michelle McAvoy, Paul Sihvonen-Binder, and Pierre Albisser have not just shown themselves to be real friends but they have acted more like family. Thank you. I can never repay you for your support and real help. I am in your debt.

Finally, I would like to thank my family for their encouragement during this research program.

List of symbols

3D Three-dimensional

μm micrometre, 10^{-6}meter

μW microwatt, 10^{-6} Watt

Ω Ohm

A area

BaTiO3 Barium titanate

BLE Bluetooth low energy

BS British Standards

^{0}C degrees centigrade

C capacitance

CB carbon black

CH2 Methylene

cm centimetre, 10^{-2} metre

CNT/PP carbon nanotubes/ polypropylene

CuS Copper Sulphide

d distance

DC Direct current

DMA dynamic mechanical analysis

DSC differential scanning calorimetry

DWNT double-wall carbon nanotubes

$\boldsymbol{\varepsilon_0}$ electric constant (vacuum permittivity)

$\boldsymbol{\varepsilon_{rf}}$ relative static permittivity (dielectric constant) (approx. 8.854×10^{-12} F·m^{-1})

F Farad

FEM finite element method

FTIR Fourier transform analysis

HDPE high density polyethylene

Hz Hertz

ITO Indium tin oxide

kΩ kiloOhm,10^3 Ohms

kV kilovolt, 10^3 Volt

LED light emitting diode

LC inductor-capacitor

m metres

m^2 square metres

m^3 cubic meter

mA milliampere, 10^{-3}Amper

mm millimetre, 10^{-3}meter

MHz Mega Hertz, 10^{6}Hertz

MPa Mega Pascal, 10^{6} Pascal

ms millisecond, 10^{-3} second

mW milliwatt, 10^{-3} Watt

mV$_{p-p}$ millivolt peak to peak

NCC nearest centroid classifier

NH2-DWCNT amino modified double-wall carbon nanotubes

nW nanowatt 10^{-9}Watt

PA-11 polyamide 11

PEDOT/PSS poly(3,4-ethylenedioxy-thiophene)/poly(4-styrenesulfonate)

pF picofarad, 10^{-9}Farad

PP polypropylene

Pt platinum

P(VDF70-TrFE30) poly(vinylidenefluoride-trifluoroethylene)

PVDF polyvinylidene fluoride

PZT lead zirconate titanate

PZT-5A lead zirconate titanate equivalent to Navy Type II (MIL-STD-1376B) Military Standard

RF radio frequency

rpm revolutions per minute

Rs real (ohmic) part of the resistance

SEM scanning electron microscopy

SiO_2 Silicon dioxide

SR silicone rubber

UV ultraviolet

V Volt

V_{p-p} peak to peak voltage

Vf overall filament volume

W Watt

XRD x-ray diffraction

Xs imaginary part of the impedance

ZnSnO3 zinc stannate

Zr/Ti Zirconate/ Titanate

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Chapter 1 Introduction

Energy harvesting materials and systems have emerged as a prominent research area that continues to grow at rapid pace (Kong et al., 2014). The main reasons behind this trend have to do with the continued miniaturization of electronic devices, such as portable electronics, sensors, and transmitters that allows for usage these electronics in applications that were previously incommodious and inefficient. Such applications include but are not limited to wearables, implantable devices and wireless sensor networks (military/ civilian applications).

What these applications have in common is the requirements/ restrictions imposed on the power supply. Power supplies need to be portable, light, to have small dimensions (comparable to the systems they are powering) and in several of the applications they should preferably be able to provide uninterrupted power without the need for replacement.

Implantable devices and wireless sensor networks are two prominent examples that showcase this fact. In the case of the implantable devices the need for a power source that will require minimum maintenance after installation is self-evident. In the case of wireless sensor networks the dispersion, number of the sensors, hence projected cost, and in certain applications the difficulty of approaching their location imposes these restrictions on the power source (Li et al., 2014; Priya and Inman, 2009).

Piezoelectric materials are very good candidates as energy sources for those applications and for other applications that do not fall in the extremes of implantable devices such as smart textiles and especially wearable applications.

Fabrication of wearable smart textiles imposes significant restrictions and requirements onto the electrically active components that will be integrated into the textile structure (whether truly integrated or simply “pasted” on). These restrictions can be briefly described as the need for ruggedness of the components (e.g. circuitry) defined as durability in mechanically demanding environments during fabrication and use of smart textile in daily life as well as unaltered comfort and washability by the integration of electronic circuits. Regarding the power supply it should be light-weight and have a high capacity to ensure uninterrupted use of the smart textile for a reasonably long time and not to compromise the comfort parameters (Cherenack and van Pieterson, 2012)

Piezoelectric materials are divided into four categories: ceramics, single crystals, polymers, and composites (the composite material is a combination of piezoelectric ceramics or single crystals with polymers). When considering the materials in a historic perspective, single crystals and ceramics were the oldest materials used for piezoelectric applications with quartz being one of the oldest materials used (Curie and Curie, 1880).

Piezoelectric polymers are the most recent materials to be investigated (Hayakawa and Wada, 1973; Kawai, 1969) and piezoelectric melt spun textile fibres started appearing in published research since approximately 2010 (Siores et al., 2010). The development of piezoelectric textile fibres leads to appealing opportunities of innovation in energy harvesting especially for wearable smart applications. The abilities offered for full integration of the piezoelectric elements to the textile substrate would resolve some the challenges mentioned in the previous paragraphs.

This PhD project aims to investigate the electrical properties of piezoelectric melt spun textile fibres with regards to their use in wearable smart applications.

1.1 Research objectives

While piezoelectric polymer films have been under investigation since 1969 when Kawai reported large piezoelectricity effect in PVDF films, textile piezoelectric melt-spun fibres are quite a recent addition to the piezoelectric material range with an appearance in literature around 2010 (Hagström et al., 2014; Siores et al., 2010). These materials are geared, by design, towards applications that incorporate smart textiles especially concerning energy harvesting from renewable, ambient energy sources. These sources may include wind, rain, waves etc as well as voluntary and involuntary human motion.

The materials used for this research project were produced using the method developed and standardised at the University of Bolton by Siores, Hadimani and Vatansever in 2010. This project aims to study the behaviour of the materials in real use conditions by investigating the durability of the materials with regards to the effect of a common cleaning/ care process applied to textiles - keeping in mind the implied interest in energy harvesting applications of smart textiles and to determine the efficiency of the materials with regards to the electrical power produced by them individually (single fibres) as well as the electrical behaviour of fabrics produced using these materials.

To accomplish the research aims the following objectives were developed:

- To investigate the effect of the washing procedure on the electrical response of the fibres
- To identify and investigate the methods that are used for the determination of the efficiency of piezoelectric melt-spun fibres
- To develop a method/ apparatus to classify the fibres regarding their efficiency in the production of electric power

- To investigate and model the capacitive behaviour of 3D weft knitted fabrics incorporating the piezoelectric melt-spun fibres.

Chapter 2 Literature review

2.1 Energy harvesting

Energy harvesting or energy scavenging as it is also known is the process by which ambient energy is captured and converted to electric energy. Power harvesting from sources such as wind, water and sun has been in existence for centuries. While these processes, in modernized form, can produce power measured in Mega Watts they are not suitable for the micro environment that consists of today's electronic systems/ devices. In this micro environment, the need is for small, portable/ wearable, light, and low energy power sources (Raju and Grazier, 2008).

Further limitations on the size and functionality of micro electronic systems can be set in place by the applications themselves. For example, in biomedical applications the main considerations are size, power source longevity and properties like heat dissipation. Moreover, considering the trend towards portable electronic devices of diminishing size culminating into the wearable electronics applications the need for long lasting, portable power sources - as a replacement to bulky, non-efficient typical batteries becomes evident (Starner and Paradiso, 2004).

Micro-energy harvesting sources include but are not limited to photonic, vibrational, electromagnetic (RF), and thermal (Steingart, 2009). Regarding the vibrational harvesting sources, the three, basic, vibration-to-electric energy conversion mechanisms are the electromagnetic (Beeby et al., 2004; Glynne-Jones et al., 2004; Perez-Rodriguez et al., 2005), electrostatic (Despesse et al., 2005; Meninger et al., 2001; Mitcheson et al., 2003), and piezoelectric (Li et al., 2002; Roundy and Wright, 2004; Umeda et al., 1997) transduction mechanism (Williams and Yates, 1996). The maximum power density from the three methods is theoretically comparable (Beeby et al., 2006). However, sub-millimetre and wafer-scale implementations are difficult for electromagnetic systems, and electrostatic systems require a polarizing charge/voltage, large motion amplitudes, and suffer from parasitic capacitances (Shad Roundy, 2005). It follows that, the research interest has concentrated towards piezoelectric transductions, specifically electrical power generation from vibrations (Anton and Sodano, 2007; Priya and Inman, 2009)

2.1.1. Energy harvesting using piezoelectric materials

Energy harvesting attempting to capture mechanical movement energy through piezoelectric generators has been extensively investigated. Human motion whether voluntary (walking) or involuntary (respiration) has long been considered as a potential source of “wasted” energy that could be harvested and used for powering wearable electronics. Human motion is characterized by large-amplitude movements at low frequencies.

The first attempts to harvest the energy produced by walking (the striking of the heel and the flexing of the ball of the foot) were carried out by the team of Kymissis, Pradiso and Shenck (Kymissis et al., 1998; Shenck, 1999; Shenck and Paradiso, 2001) at the Massachusetts Institute of Technology (MIT). Kymissis et al. (Kymissis et al., 1998) investigated three different approaches for harvesting the energy produced by walking. A rotary magnetic generator and a PZT (piezoceramic material) actuator both placed in the heel of two different sneaker shoes in order to exploit the impact energy during walking, while a PVDF insole (stave) was used to exploit the bending motion of the sneaker sole.

Regarding the performance of the three approaches it was found that the average power produced by the PVDF stave and the PZT actuator (with a 250KΩ load) were 1mW and 1.8W respectively, while the magnetic generator produced an average of 0.23W, with a load of 10Ω. As was mentioned in the discussion of their results, the paper did not investigate any way of transferring the power produced away from the shoe. In his MSc thesis, Shenck used a PZT bimorph, placed in the heel area of a sneaker. The bimorph was stated to be able to produce an average power of 8.4 mW with a load of 500kΩ. In their 2001 paper Shenck and Paradiso (2001) investigated a power storage circuit which was designed to power a radio frequency (RF) tag which was also mounted on a shoe and an offline forward switching DC-DC converter was developed.

Mateu and Moll (2005) in their 2005 paper analysed the majority of the previous attempts to utilize piezoelectric (PVDF) cantilever beam inserts for energy harvesting – with specific mention to the work of Kymissis, Shenck and Paradiso. The aim of their work was to model the optimum configurations for this type of energy harvesting inserts. Similarly, Yoon et al. (2005) designed, modelled, and optimized curved piezoceramic unimorphs for use as heel inserts in shoes.

Häsler et al. in their in vivo research (1984) investigated a power scavenging mechanism utilizing implantable PVDF films which capture energy produced by the displacement of the ribs during breathing. Hausler and Stein implanted the device in a dog and measured a peak voltage of 18 V and an output power of 17 μW. Ramsay and Clark (2001) carried out an in vivo research as well utilizing an implantable power scavenging device that uses a square PZT-5A membrane to extract energy from fluctuating blood pressure.

The modelling results show that a maximum power of 2.3 μW can be obtained by maximizing the area and minimizing the plate thickness (range of thicknesses investigated were 9 to 1100μm). Further in the use of blood pressure fluctuation as a source of energy to be harvested by piezoelectric PVDF membrane plates (circular and square) Sohn et al. (2005) used finite element method (FEM) to model the power generation behavior. According to this model a circular diaphragm with a 11.2 mm diameter and an optimum thickness of 9mm can produce 0.61 μW. The results obtained from the FEM were verified by comparison with the results of the theoretical analysis. Furthermore, experiments were carried out by pulsing actual membranes at a 60Hz frequency. The circular membranes produced 0.34 μW, while the square membranes produced 0.25 μW

2.2 Piezoelectricity

Piezoelectricity, discovered in 1880 by Pierre and Jacques Curie in quartz (1880), is observed in all materials with a crystalline anisotropy. Piezoelectricity has two distinct effects. The direct effect is the polarization of the material under a mechanical stress and the inverse effect corresponds to a mechanical displacement when electric polarization is applied to the material (Jean-Mistral et al., 2010)

Piezoelectric materials belong to the general group of dielectric materials, electrical insulators that can be polarized by an applied electric field (Figure 1). Piezoelectric materials are non-centrosymmetric dielectrics; this means that when subjected to an external electric field, there will be asymmetric movement of the neighbouring ions, resulting in significant deformation of the structure; this deformation is directly proportional to the applied electric field. (Abramovich, 2016).

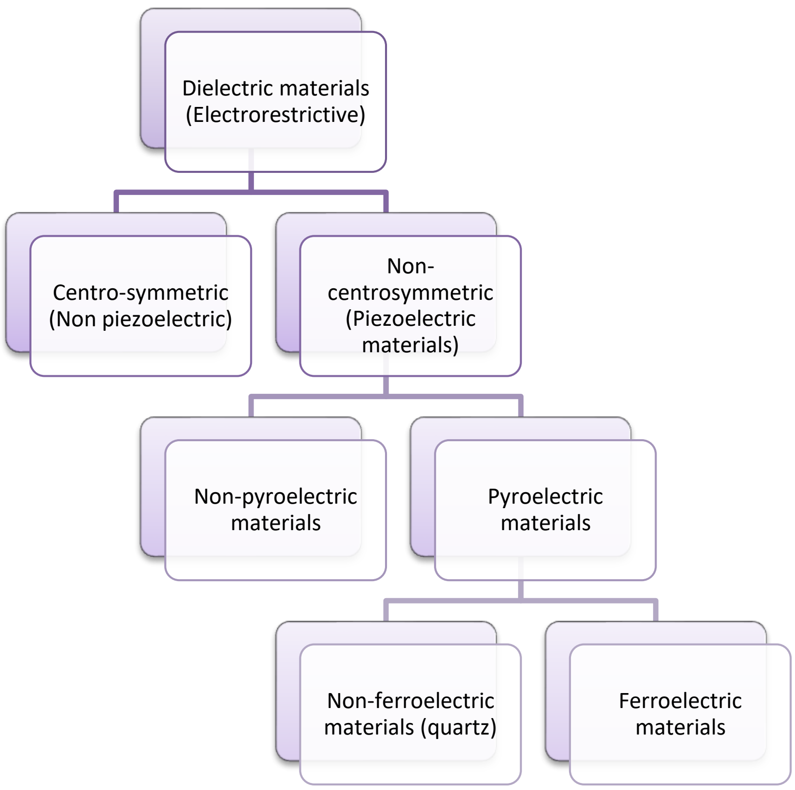


Figure 1. Classification of dielectric materials

Pyroelectricity, the ability of certain materials to generate an electrical potential when they are heated or cooled, occurs in all materials that belong to a polar crystal symmetry class. It should be noted that, not all non-centrosymmetric classes are polar, not all piezoelectric crystals are pyroelectric. However, all pyroelectric crystals are piezoelectric. Ferroelectrics form a subset of the set of pyroelectrics because they are polar materials in which the direction of the polar axis can be changed by the application of an electric field. (Whatmore, 1991)

Investigation into the piezoelectric properties of materials commenced from materials readily available in nature such as carnauba wax (Eguchi, 1925), wood (Fukada, 1955) and bone (Fukada and Yasuda, 1957). In 1946, it was shown that $BaTiO_3$ ceramic, can be made piezoelectric by an electrical poling process. The first commercial piezoelectric devices based on $BaTiO_3$ ceramics were phonograph pickups and appeared on the market about 1947 (Berlincourt, 1981). An advance of great practical importance was the discovery in 1954 of very strong piezoelectric effects in lead zirconate titanate solid solutions (PZT)(Ramadan et al., 2014). PZT piezoceramics replaced $BaTiO_3$ ceramics in most applications and PZT remains one of the most popular piezoceramic materials.

PZT is a polycrystalline ferroelectric material. In a ferroelectric material, the internal dipoles of the material can be reoriented by the application of an external electric field, leaving a remnant polarization at zero applied electric field (Setter et al., 2006). This remnant polarization also changes with the applied stress and this is how piezoelectricity takes place. Since 1954 there has been a lot of research to determine the effects of composition (Zr/Ti) and small amounts of additives on the electrical and mechanical properties of PZT piezoceramics (Heywang and Thomann, 1984; Jang, 2000)

In 1969 Kawai (Kawai, 1969) discovered large piezoelectricity in elongated and poled films of polyvinylidene fluoride (PVDF). Research has shown that the polar β-phase of PVDF, which is caused by the application of mechanical stress and/or strong electric fields, is responsible for the development of the piezoelectric property of the material (Davis et al., 1978; Sencadas et al., 2009).

The piezoelectric behaviour of other polar polymers like the odd numbered polyamides such as Polyamide 11, have also been investigated (Newman et al., 1980, 1990; Takase et al., 1991). Newman et al investigated the crystal structure of Polyamide 11, as well as the effect of poling conditions (temperature, time, and poling field) to the overall piezoelectric constants of the material. Polyamide (Nylon) is a polymer consisting of the zig-zag chains of CH2 groups connected by the amide groups (H–N–C=O). The planar sheet structure of molecules is formed by hydrogen bonds between amino groups of adjacent molecules. Scheinbeim et al. (1992) used X-ray diffraction to investigate the orientation of the inter-chain hydrogen bonds between the amide bonds, which make up the sheet structure of Polyamide 11, when investigating the polarization of Polyamide 11 in film form. The planar sheets are oriented parallel to the surface of the film. According to their findings, during poling the amide dipoles rotate 90º under the strong electric field, which also causes the 90º rotation of the hydrogen bonded sheets. This rotation results in the 180º rotation of the dipoles.

The molecular structure of odd numbered (top) and even numbered (bottom) polyamides can been in Figure 2. In odd-numbered nylons, the electric dipoles formed by amide groups (H–N–C=O) are sequenced in a way that all the dipoles are in the same direction. Therefore, a net dipole moment occurs. In even-numbered nylons, one amide group is in one direction, the next one will be in the opposite direction, alternately. This results in an intrinsic cancellation of the dipole moments (Su, 2007).

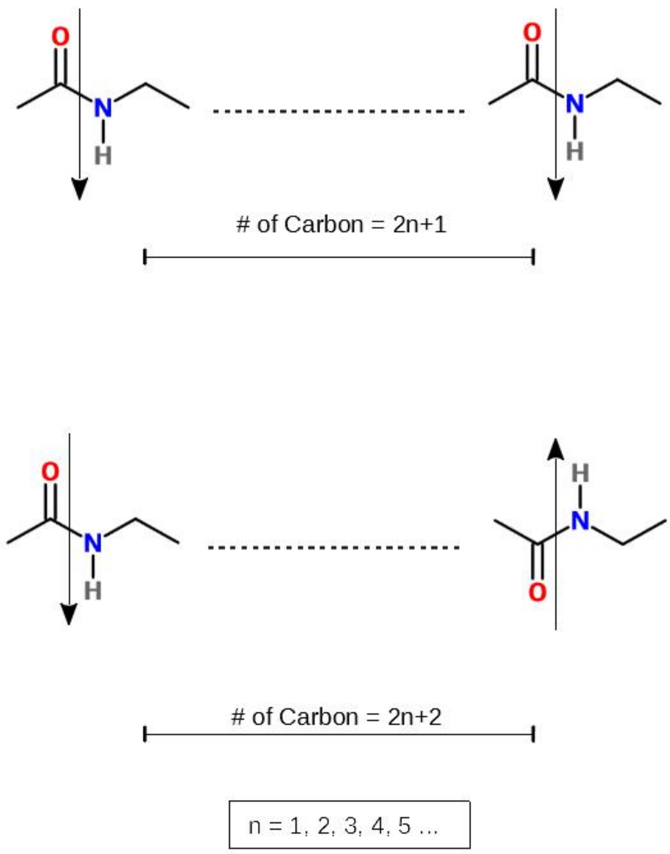


Figure 2. Schematics of molecular structure of odd-numbered and even-numbered polyamides

The piezoelectric behaviour of polypropylene has mostly been investigated in the case of cellular polypropylene films (Hillenbrand and Sessler, 2000; Jukka Lekkala et al., 1996; Neugschwandtner et al., 2000; Paajanen et al., 2000; Peltonen et al., 2000; Sessler and Hillenbrand, 1999), where piezoelectric behaviour is a result of the morphology of the structure (air or other gas filled voids, void morphology, and charge distribution. Other research on the piezoelectric properties of single film polypropylene or melt-spun polypropylene fibres has been scarce. Research carried out by Kravtsov et al. (2002) investigated polarization of melt-spun polypropylene fibres and concluded that melt-spinning technology favours formation of spontaneous electret charge in the fibres and that forced fibre polarization in external electric fields gives rise to strong electret effect.

More over in the same paper Kravtsov at al. attributed the total electret effect in polypropylene fibres to mechanisms such as Maxwell–Wagner polarization, dipole orientation and charge carrier injection. Furthermore in 2015, Klimiec et al. (2015)investigated the effect of the introduction of SiO_2 and Kaolin filler on the piezoelectric constant and thermal durability of polypropylene electret, by creating a cellular structure in a single layer film.

In the research quoted above most of the polymeric piezoelectric materials under investigation were in film form, however, it is now possible to use polymeric piezoelectric filaments (Hadimani et al., 2013; Siores et al., 2010)for the applications where flexibility is required. For example, in the interest of producing innovative, “smart” textile products whose components can be integrated into existing textile structures (Siores et al., 2011; Soin et al., 2014; Derman Vatansever et al., 2011).

While use of piezoceramic materials such as PZT is extensive, piezoceramics are extremely brittle. Lee et al. (2004) compared a PVDF film coated with poly(3,4-ethylenedioxy-thiophene)/poly(4-styrenesulfonate) [PEDOT/PSS] electrodes to films coated with the inorganic electrode materials, indium tin oxide (ITO) and platinum (Pt). When subjected to vibrations of the same magnitude over varying frequencies, it was found that the films with the inorganic coated electrodes begun to show fatigue cracks at an early stage and at relatively lower frequencies than the PEDOT/PSS film. In further research by Lee et al. (2005) piezoceramics tested were susceptible to fatigue crack growth when subjected to high frequency cyclic loading.

Moreover, while ceramics have a higher piezoelectric constant, the polymers are more flexible making them more appropriate for areas such as wearable applications (Vatansever et al., 2012b). Wearable applications, smart textiles, and e-textiles in general (multifunctional textile products) place specific limitations regarding the rigidity, elasticity, thickness, wearability, comfort etc. of the usually fibrous materials to be incorporated in the product, hence the need for piezoelectric material forms that emulate classic textile structures (fibres, yarns, fabrics). Multifunctional textile materials become increasingly important for combined applications. Piezoelectric fibres and yarns open a new field in the multifunctional textile area, especially for energy harvesting applications. It is expected that soon a garment using piezoelectric fibres will be developed capable of producing usable electrical power (Jost et al., 2014).

2.3 Melt-spun textile fibre materials as piezoelectric elements

In order to obtain usable textile filaments (filaments are a synonym of the word fibre and are specific to continuous fibres vs staple fibres) from polymers such as PVDF, the polymer must go through a process known as spinning, i.e. the transformation (ordering) of the material into yarn. There are several spinning methods applied to polymers that are already in use in the textiles sector. All methods consist of transforming a solution of the polymer, either produced directly from raw materials (direct spinning) or from dissolving/ melting the polymer chips (dry spinning, melt spinning, electrospinning).

Both melt spinning, and electrospinning can be utilized to produce piezoelectric polymer filaments. The present research is concerned with filaments produced through melt spinning. In melt spinning polymer chips are melted and then the melt is forced (extruded) through the spinning head called a spinneret. The holes of the spinneret can have different cross-sectional shapes such as round, trilobal, pentagonal etc. Each of the cross-sectional shapes has its own advantages regarding the appearance or properties of the filaments produced. Another available fibre structure is the production of bicomponent filaments. Most of the papers analysed below are concerned with bicomponent filaments. After production, the filaments are drawn and wound unto bobbins. The drawing (elongation) results in orientation of the macromolecules of the polymer and improves fibre characteristics such as tensile strength. (Cook and Cook, 2005; Mohammadi et al., 2007).

The process of producing piezoelectric melt spun textile fibres as described mainly for PVDF includes one more stage after the final drawing stage used during production of the melt spun fibre. That stage, poling is a combination of extension, heating, and exposure to high voltage. Extension of the polymer structure (drawing) together with an elevated temperature allows for transformation of the α-phase crystallites to β-phase. Then, to orient the dipole moments of the β-phase crystallites (render the structure polar), PVDF is subjected to a high electric field. In the specific case of PVDF the stretch ratio and the temperature at which poling is realised affect the maximum β-phase content, which is as previously discussed directly responsible for the development of the piezoelectric property of PVDF (Eguchi, 1925). Typical conditions of poling are 80-90 ^{0}C and drawing ratio of 5:1 (Gomes et al., 2010; Murase and Nagai, 1994; Sajkiewicz et al., 1999; Sobhani et al., 2007).

Figure 3 displays the continuous method for the production of melt spun piezoelectric textile fibres developed at the University of Bolton. A single screw laboratory line melt extruder originally constructed by Plasticisers Engineering, UK is used for melt extrusion of the piezoelectric fibres. The extruder screw has a diameter of 22 mm, which can be operated at speeds of up to 50 rpm though a reduction gear mechanism. The polymer is fed through the screw at speeds of 2 rpm. For all the polymers, a flat temperature profile is maintained wherein the hopper temperature is kept at 190°C with a 10°C increment along the barrel and the die head temperature being set at 230°C. The extrusion line has two water cooled take-up slow rollers, 4 temperature controlled slow rollers and 2 fast rollers. The water-cooled rollers are used for the additional cooling of the fibre and temperature-controlled rollers heated the fibre to the required poling temperature, 80 °C in this case. The space between temperature controlled slow rollers and the fast rollers housed a pair of flat-plate electrodes separated by a gap of 10 mm.

The electrodes are connected to a Spellman SL300 series high voltage power supply with a range of 0-20kV at an output current of 3mA. The bottom electrode is also heated to maintain the poling temperature at 80°C during the polarization step where the fast rollers' speed is maintained at 5 times faster than that of the slow rollers to obtain a draw ratio of 5:1 and a high voltage of 13kV is applied. The poling conditions (temperature, extension, and high voltage) are applied simultaneously on the fibres between the temperature controlled slow rollers and fast rollers (Matsouka et al., 2017b)]

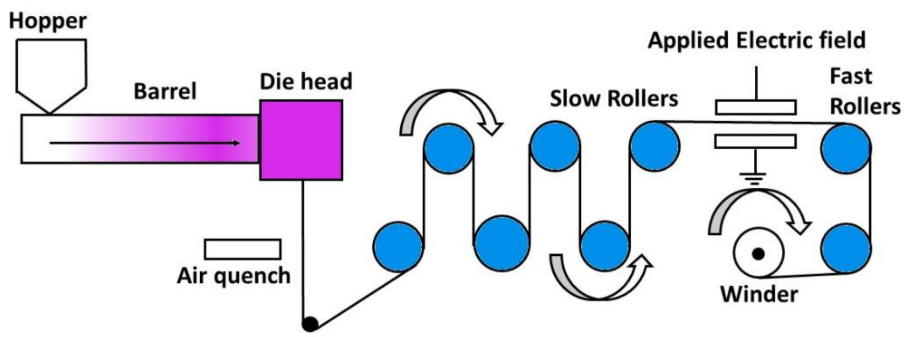


Figure 3. Schematic of continuous method of production of piezoelectric melt spun fibres

There currently exist two patent applications regarding the production of piezoelectric melt spun piezoelectric fibres. The first one by Siores et al. (2010)is concerned with the production of a fibre of solid cross-section and a substantially homogeneous composition while the one by Hagström et al. (2014) refers to the production of a fibre comprising of a core made of an electrically conductive flexible thermoplastic composite comprising at least of one polymer and at least one conductive filler and a surrounding material enclosing the core material made of a permanently polarizable polymer.

Reviewing the results of the bibliographical search, regarding melt spun textile piezoelectric fibres, it became evident that certain research papers could be considered part of a continuing study into this subject by a specific research team. Due to the number of researchers working in each team the presentation of the papers that were studied will be geographically grouped (location of the organisations involved in the research).

In Sweden research into melt spun piezoelectric textile fibres has resulted in a patent (Hagström et al., 2014) and a number or research papers. The first paper, chronologically, by Lund and Hagström (2010), investigated the influence of spinning parameters on the β-phase crystallinity of PVDF yarns with no additives or conductive cores. Beginning with the next paper again by Lund and Hagström (2011) the researchers introduced the concept of bicomponent PVDF fibres (i.e. PVDF filaments with a conductive core). The conductive cores used in the research originating in Sweden included electrically conductive composites of carbon black (CB) and high-density polyethylene (HDPE) (Lund and Hagström, 2011; Nilsson et al., 2013), either non-functionalized or amino-functionalized double-wall carbon nanotubes (DWNT) (Lund et al., 2011) and ethylene-octane copolymer and CB or a high-density polyethylene and again CB (Lund et al., 2012). Guo et al. (2013) carried out a comparison between three compositions of piezoelectric fibres based on PVDF, i.e. PVDF fibres, PVDF/ nanoclay fibres and PVDF/NH2-DWCNT (amino modified double wall carbon nanotubes). Finally, in a paper by Nilsson et al. (2014) the composition of fibres under investigation is given as bicomponent with a PVDF sheath and a conductive core while pointing at a previous paper (Lund and Hagström, 2011) for more information. Concerning the methods used for characterisation of the fibres (filaments) examined in the above papers these are as follows.

Table 1. Characterisation methods used in research papers originating in Sweden

Method	**Research papers**
Differential scanning calorimetry (DSC)	(Lund and Hagströn, 2010, 2011; Nilsson et al., 2013)
X-ray diffraction (XRD)	(Lund et al., 2011, 2012, Lund and Hagström, 2010, 2011)
Determination of tensile strength to break	(Lund et al., 2012; Lund and Hagström, 2010; Nilsson et al., 2013) *
Determination of viscosity as a function of shear rate	(Lund et al., 2012)
Electrical (DC) conductivity measurements	(Lund et al., 2012; Nilsson et al., 2013)
Determination of the resistance and capacitance of the sensor (individual filament lengths oriented in parallel) and electromechanical characterisation of the sensor by subjecting it to a dynamic compression strain perpendicular to the fibre axis	(Lund et al., 2012)
Determination of the electric signal and strain of a yarn comprising of 24 fibres by subjecting it to a	(Nilsson et al., 2013)

dynamic tensile strain parallel to the fibre/ yarn axis and estimations of the mean power from the fibres	
Evaluation of the sensor (yarn woven into fabric) properties for heartbeat detection	(Nilsson et al., 2013)
Characterisation of the piezoelectric fibres by connecting the fibre to an impedance analyser.	**(Nilsson et al., 2014)**

*testing carried in yarn form

Regarding the research originating in the UK; in 2011, Vatansever et al (2011), published a chapter in the book “Smart Woven Fabrics in Renewable Energy Generation” and the chapter included a presentation of the production method for PVDF piezoelectric monofilament yarns. In 2012, Vatasnaver et al, (2012a) presented the production process of a PA-11 (Polyamide 11) piezoelectric monofilament yarn. Vatansaver et al. (2011) and Hadimani et al. (2013), investigated the properties of a PVDF monofilament yarn. In 2015 Bayramol et al. (2015), investigated the effect of addition of multiwalled carbon nanotubes on the piezoelectric properties of polypropylene filaments.

The UK based research constitutes the only research that investigated materials other than PVDF, namely PA-11 (Vatansever et al., 2012a)and Polypropylene (Bayramol et al., 2015). They also hold the oldest patent (Siores et al., 2010)on the production of piezoelectric melt-spun textile filaments, the process described in detail by Hadimani et al. (2013). Vatensever et al. (Vatansever et al., 2012a) touches on the subject of the amount of energy produced by a single filament vs the energy required for powering small electronic devises, though without providing specific data regarding the energy produced.

Table 2. Characterisation methods used in research papers originating in the UK

Method	**Research papers**
Fourier transform infrared spectroscopy (FTIR)	(Hadimani et al., 2013)
X-ray powder diffraction (XRD)	(Hadimani et al., 2013)
Determination of linear density	(Hadimani et al., 2013; D. Vatansever et al., 2011)
Determination of tensile strength	(Bayramol et al., 2015; D. Vatansever et al., 2011)
Examination of the micro structures of the filaments under scanning electron microscope (SEM)	(Bayramol et al., 2015; Hadimani et al., 2013; D. Vatansever et al., 2011)
Determination of the electric response in Volts of a group of fibres when stimulated by a mechanical stimulus (impact)	**(Bayramol et al., 2015; Derman Vatansever et al., 2011; D. Vatansever et al., 2011; Vatansever et al., 2012a)**

In Germany, in 2010, Walter et al (2010) manufactured melt-spun PVDF fibres of textile finesse. Apart from the typical production processes, the produced filaments underwent false twist texturizing. In 2011 Steinmann et al. (2011), produced melt-spun PVDF textile fibres using different production parameters. Also in 2011, Walter et al (2011) carried out characterisation of composites made by combining piezoelectric PVDF monofilaments with a two-composite epoxy resin. In 2012, Walter et al (2012) further developed the previous research project (Walter et al., 2010)by producing both a warp knitted fabric and two woven fabrics (plain and twill weave). In 2013 Glauß et al (2013), investigated the spinability and characteristics of PVDF bicomponent fibres with CNT/ PP core. This research project related to research done by Steinmann et al (2013) on the extrusion of CNT-modified polymers. In 2015 Glauß et al (2015) worked on the production and functionalizing of bicomponent fibres consisting of PVDF “sheath” and conductive CNT/PP core.

Also in 2015 Glauß et al (2015)presented their research in the 4th International Conference on Materials and Applications for Sensors and Transducers. The presentation regarded the poling effect on bicomponent piezoelectric fibres (PVDF sheath with carbon nanotubes core).

The research by Steinmann et al. (2011) into the phase transitions of melt-spun PVDF fibres was a significant step in determining the effect of process parameters on the crystallinity of PVDF. The aim of the research was to understand the crystallization and phase transitions in PVDF fibres in order optimize the formation of the β phase (which is connected to the piezoelectric behavior of PVDF). The research resulted in a detailed overview of the effect of production properties on the phase transformations of PVDF, which can be seen in summary in Figure 4.

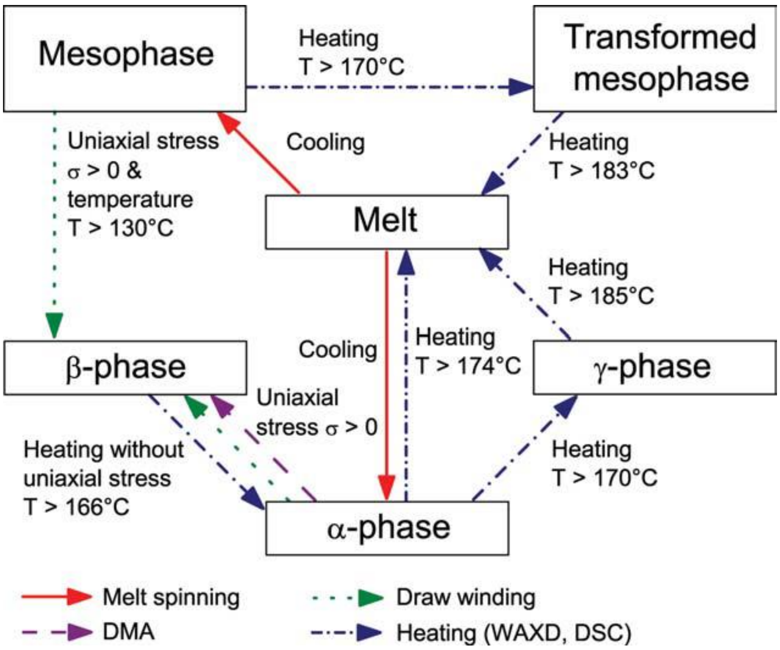


Figure 4. Possible structural phase transitions in fibrous PVDF, with the causative processing conditions and experiments indicated. (Figure reproduced from Steinman et al. (2011))

Walter et al. (2011) constructed composite specimens using a sandwich of PVDF monofilaments placed parallel to each other and an epoxy resin, placed between copper films. Polarization was carried out on the composite specimens in an oil bath. Determination of the piezoelectric behaviour of the samples was carried out both parallel and perpendicular to the fibres. The specimens were subjected to tensile strain and the voltage produced was measured. The results showed an anisotropy of the behaviour of the composite specimen regarding the voltage produced depending on the direction of the strain (lengthwise or perpendicular to the length).

Table 3. Characterisation methods used in research papers originating in Germany

Method	**Research papers**
Differential scanning calorimetry (DSC)	(Steinmann et al., 2011, 2013, Walter et al., 2010, 2011)
Wide angle, x-ray diffraction (XRD)	(Steinmann et al., 2011, 2013, Walter et al., 2010, 2011)
Scanning electron microscope SEM	(Walter et al., 2010)
Determination of yarn finesse	(Walter et al., 2010)
Determination of tensile strength at break	(Walter et al., 2010, 2011)
Determination of hot air shrinkage	(Walter et al., 2010)
Dynamic mechanical analysis (DMA)	(Steinmann et al., 2011)
Monitoring of the formation of surface charges on the composites under tensile and bending deformation	(Walter et al., 2011)
Rheometry measurements	(Steinmann et al., 2013)
Transition electron microscopy	(B. Glauß et al., 2015; Steinmann et al., 2013)

Determination of specific resistivity	(B. Glauß et al., 2015; Steinmann et al., 2013)
Bright field microscopy	**(Steinmann et al., 2013)**

In Portugal, in 2011, Ferreira et al (2011) investigated the effect of processing conditions and a conductive inner core on the electroactive phase content and the mechanical properties of PVDF filaments without a core and with a core containing a conductive PP (polypropylene)/Carbon black composite. In 2013 Silva et al (2013) investigated the effect of repeated processing cycles on crystallinity and electroactive phase content of recycled PVDF filaments. In 2014 Martins et al (2014) examined the properties of piezoelectric coaxial filaments. The test specimens comprised of a piezoelectric cable obtained from a two-layer coextruded filament, comprising an internal semi conductive electrode (carbon-black filled polypropylene compound and a carbon nanotube-based compound) and a PVDF layer, coated with a thin layer of a semi conductive copper-based lacquer. Also in Portugal, in 2014, Rui et al. (2014) investigated coaxial PVDF filaments with a filament core comprising of conductive PP. Ferreira et al. (2011) concentrated their efforts in producing coaxial piezoelectric filaments made from PVDF, as opposed to pure polymer filaments. The use of a conductive PP/carbon black composite core in the filaments is a common approach in other research for instance the work by researchers based in Sweden (Guo et al., 2013; Lund et al., 2011, 2012, Nilsson et al., 2013, 2014) and in Germany (Glauß et al., 2013; Benjamin Glauß et al., 2015; B. Glauß et al., 2015).

The subject of the research by Silva et al. (2013) (recycled PVDF filaments) was unique in the literature reviewed. The results of several consecutive processing cycles on piezoelectric PVDF samples showed that all the parameters that were studied were unaffected or only very slightly affected by up to 9 processing cycles suggesting that PVDF recycling was feasible regarding its electroactive properties.

Table 4. Characterisation methods used in research papers originating in Portugal

Method	Research papers
Wide angle, x-ray diffraction (XRD)	(Ferreira et al., 2011; Silva et al., 2013)
Tensile strength tests to determine the Young modulus of the fibres	(Ferreira et al., 2011)
Fourier transform infrared spectroscopy (FTIR)	(Martins et al., 2014; Silva et al., 2013)
Determination of tensile strength at break	(Martins et al., 2014; Rui et al., 2014)
Measurement of the electric conductivity	(Martins et al., 2014)
Measurement of the electromechanical response (Voltage response of the filaments during mechanical stimulation [tensile strain]),	(Martins et al., 2014)
Microscopy	(Martins et al., 2014)
Determination of the electromechanical response of the filaments (voltage produced due to mechanical stimulation (vibration, elongation)	**(Rui et al., 2014)**

In France, Kechiche et al. (2013) investigated the properties of a piezoelectric coaxial filament, which had a sheath of P(VDF70-TrFE30) (poly(vinylidenefluoride-trifluoroethylene)) and a copper monofilament as core. Their work was based on previous research carried out by Khoffi et al (2011) on the production of a polyethylene terephthalate/copper composite filament.

In a joint paper by researchers based in Australia and Germany, Magniez et al. (2013) investigated the effect of drawing on the molecular orientation and polymorphism of melt-spun PVDF fibres. The methods used for the characterisation of the fibres were, i) determination of tensile properties of the fibres, ii) XRD, iii) FTIR, iv) determination of molecular orientation using optical birefringence, v) determination of the electric response (Voltage) of the piezoelectric fibres integrated in to a woven textile structure after mechanical stimulation (compression).

The approach by Kechiche et al. (2013) of manufacturing and studying a coaxial filament(PET/copper) was found to be innovative in the literature reviewed. The research team had to design and develop, a new type spinneret to provide a good centring of the inner core(copper filament) in the P(VDF70-TrFE30) matrix copolymer. The research team were able to integrate the monofilament yarns into a woven fabric structure and use the resultant fabric as a pressure sensor.

Table 5. Characterisation methods used in research papers originating in France/ joint paper from Australia & Germany

Method	**Research papers**
Differential scanning calorimetry (DSC)	(Khoffi et al., 2011)
Wide angle, x-ray diffraction (XRD)	(Khoffi et al., 2011; Magniez et al., 2013)
Fourier transform infrared spectroscopy (FTIR)	(Magniez et al., 2013)
Determination of tensile strength	(Khoffi et al., 2011; Magniez et al., 2013)
Determination of the sensing capabilities of a woven fabric incorporating the coaxial filaments (voltage response to compression)	(Khoffi et al., 2011)
Determination of molecular orientation using optical birefringence	(Magniez et al., 2013)

Determination of the electric response (Voltage) of the piezoelectric fibres integrated in to a woven textile structure after mechanical stimulation (compression)	**(Magniez et al., 2013)**

In 2012 Vassiliadis et al. (2012)measured the electric properties, of certain piezoelectric fibres, namely, PVDF, PP and PA-11, when stimulated mechanically by a peg fixed on a shaft with a varied speed of rotation. The measurements taken using this experimental set up, included the peak to peak voltage produced by the fibres under that varied stimuli. In 2013 Vossou et al (2013) carried out a computational investigation of the mechanical behaviour the same piezoelectric fibres as Vassiliadis et al. (2012). In that paper, modal analysis of a piezoelectric fibre was performed with the use of the finite elements method to evaluate its eigenfrequencies and mode shapes (modal analysis is the study of the dynamic properties of systems in the frequency domain; a typical example would be testing structures under vibrational excitation).

Furthermore, by comparing the diagram produced by plotting the bending, y-axis, reaction moment, developed at the clamped end of the fibres versus time to the diagram of the deflection of the free end of the fibres it was found that the diagram of the bending, y-axis, reaction moment resembled strongly the typical waveform produced during periodic stimulation of piezoelectric ribbon fibres plotting voltage versus time. These findings suggest that the production of electric power through the stimulation of the fibres is confined to the clamped area of the fibre i.e. the specific area of the fibre that is being bended.

2.3.1 Results of the review of the research into piezoelectric textile fibres

Based on the analysis of the published literature that pertains to melt–spun piezoelectric textile fibres three conclusions can be reached i) most of the research carried out focuses on PVDF core spun fibres with very few exceptions for example the 2015 paper by Bayramol et al. (2015) that investigated the piezoelectric behaviour of PP, ii) the majority of the current research utilizes test methods such as XRD, DSC and FTIR to characterise piezoelectric fibres and iii) there is no standardized method for the determination of the electrical response of the fibres to mechanical stimulation (neither as a method nor as equipment). Methods such as XRD, DSC and FTIR aim at characterisation of the fibre crystallinity and especially in the case of PVDF, the percentage of β phase, which is the source of the piezoelectric properties for polymers.

Furthermore, regarding the characterisation of the electromechanical response of the fibres, the data offered by the literature can be summarised by noting that there are two approaches a) testing that is intended to show the potential of the fibres, i.e. qualitative tests and b) testing that measures the voltage produced by the fibres when the fibres (or multifilament yarns or fabrics incorporating said yarns) are mechanically stimulated either by tensile strain (Martins et al., 2014; Nilsson et al., 2013; Rui et al., 2014), impact (D. Vatansever et al., 2011; Vatansever et al., 2012a; Walter et al., 2011) or compression (Khoffi et al., 2011; Lund et al., 2012; Magniez et al., 2013).

From the electrical point of view, the previous research approaches reported in the cited literature restrict themselves in the measurement of the generated voltage, i.e. the various piezoelectric fibres were characterized by the maximum voltage generated. In most of the tests reported in the existing literature the measurement of the open circuit voltage without the connection of an electrical load was presented. In most cases this open circuit voltage becomes the main performance indication and ranking criterion.

However, just the open circuit voltage does not allow the full study of the piezoelectric fibre as an electrical generator i.e. it is impossible to assess the current provided by the source under operation conditions with load connected. Consequently, using only, the open circuit voltage it is impossible to estimate the true electrical power produced by the piezoelectric fibre. Furthermore, measuring both the voltage and the current generated by the specimens it can be discerned that the capacitance behaviour of the materials aka the phase difference between voltage and current measurements.

2.4 Textile-element based capacitors

The current trend for overcoming the difficulties inherent to the integration of electronic components into textile substrates involves the development and replacement of traditional electronic components by textile based materials and structures, such as conductive textiles (Balint et al., 2014; Chen et al., 2011; Das and Prusty, 2012; Park et al., 2012; Park and Jayaraman, 2003; Shirakawa et al., 1977), textile based light emitting diodes (LED) (Yang et al., 2012), transistors (Hamedi et al., 2007; Małachowski and Żmija, 2010), and sensors (Ma et al., 2014; Takamatsu et al., 2012).

There have been various attempts at constructing textile-based capacitors many of them attempting to create structures corresponding to the classical parallel plate ones. Sergio et al. (2002) described a sensor array manufactured by alternating rows and columns of isolating and conductive fibres. While the researchers proposed four different scenarios for the creation of the capacitor array, the scenario that was realized comprised capacitors that are implemented as strips of conductive fabric thermally soldered to the two opposite sides of a foam layer. Meyer et al. (2006)presented an array of textile capacitors, where the plates were separated by a spacer insert – the actual plates of the capacitors were created by embroidering with conductive thread on the fabric that formed the outer layer of the combined structure and a method for measuring muscle activity by a sensor employing two layers of spacer fabric sandwiched between two layers of conductive fabric. Eriksson et al. (2011) investigated the concept of a 3D-woven capacitive structure as a proof of concept (the woven prototype capacitor was supported between Plexiglas plates).

In the research by Yang et al. (2014)the capacitor effect was produced by silver yarn fabric that was stitched on synthetic fibre fabric and placed on a foam pad that was shaped like a prism. The combined structure was then sewn on an elastic band. The sensor was modelled as a breath sensing system. Guo et. al (2016)researched a capacitive tactile sensor (e-skin) based on a carbon black (CB)/silicone rubber (SR) composite dielectric printed on a flexible textile substrate (Polypropylene (PP) non-woven fabric), that was then covered in rubber. The design was based on screen printing of the composite dielectric on a textile substrate, to provide flexibility and wearing comfort.

Takamatsu et al. (2016) in their research trying to develop a sensing floor covering (meter-scale) with the proposed use of monitoring movement of humans (specifically the elderly) across floors, created a specialised woven structure incorporating capacitors created by overlapping wide width stripes of polyamide yarns PA, individually coated with conductive polymer of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS). The overlap of the stripes was in two layers at right angles creating a grid with sensor capabilities at the cross-sectional points.

Wijesiriwardana et al (2005) used flatbed knitting and conductive polymer yarns made from Copper Sulphide (CuS) polyester to construct capacitive fibre-meshed transducers that can be used for touch sensing. Furthermore, they constructed two sensors with electrode islands with knitted structures. The first one was constructed with parallel-plate arrangement, and it was used as a touch and compression transducer. The second one was constructed with a single-layer electrode structure and it was used as a near-field proximity sensor. For the double-layer approach, an elastic nonconductive material was used between the electrodes. Each layer was constructed separately. Wijesiriwardana suggested that the layers could be assembled by using laminating or sewing; for the prototypes presented in the specific paper sewing had been used.

Avloni et al (2008) investigated the electromagnetic interference shielding effectiveness of polypyrrole-coated polyester nonwoven textiles. The research was carried out on four non-woven samples and one twill fabric sample. A correlation between the shielding effectiveness and the surface conductivity of composites was found.

Holleczek et al. (2010) investigated and developed textile pressure sensors for sports applications. Electrodes of conductive textiles coated with silver arranged on both sides of compressible spacers made from Croslite ™ integrated three sensors into a snowboarding sock at relevant positions under the heel and the ball of the foot were used to form a capacitor. Three sensors were integrated into a snowboarding sock at relevant positions under the heel and the ball of the foot. The pressure measurement results were processed using a Nearest Centroid Classifier algorithm (NCC). After processing the results showed that the system could be used for gait analysis or the monitoring of the in-shoe pressure distribution of runners.

Meyer et al (2010), developed a textile pressure sensor for sitting posture classification. The pressure sensor comprised of two electrodes made of conductive textile, with a compressible spacer (3D warp knitted fabric) to separate them. The electrodes on one side of the sensor were single electrodes which were embroidered with conductive yarn. On the other side of the sensor there was the common electrode which consisted of a silver-coated woven textile. Most recently Potirakis et al. (2017) patented a method to produce textile capacitors by hot welding.

The challenges faced when creating a textile-based capacitor as presented in the literature are concerned with the need i) for a structure with easily customizable construction parameters and relative structural stability, and ii) the availability of a production method that should preferably not require expensive or complicated steps. A very common approach to constructing a 3D structure mimicking the conventional parallel plate capacitor as presented in the literature was the positioning of the conducting elements (whether fabric or composite material) against foam or 3D textile structures as an external (added element). This resulted in structures that were complex and not easily customizable and allowed lateral motion of the conductive layers.

Chapter 3 "Investigation of the durability and stability of piezoelectric textile fibres"

"Investigation of the durability and stability of piezoelectric textile fibres" (Matsouka et al., 2017b) (Appendix A) was published in July 2016 in the Journal of Intelligent Material Systems and Structures (impact factor 2.255). The paper subject was the investigation of the piezoelectric behaviour of polypropylene (PP), polyamide-11(PA-11) and polyvinylidene difluoride (PVDF) melt spun piezoelectric textile fibres in terms of peak-to-peak voltage generation capabilities after a washing cycle at 40^0C with the addition of detergent as described in test method BS EN ISO 105-C06:2010 (2010).

3.1. Materials - Methods

The materials used for the research, the pristine PP, PA-11 and PVDF fibre samples, were provided by IMRI in the University of Bolton. The samples had been produced by Derman Vatensever Bayramol (2012) under the research conducted for the fulfilment of the requirements for a degree of doctor of philosophy. It should be noted that while Bayramol also investigated the properties of the yarns her approach was different as the investigation of the electromechanical response of the fibres was carried out in the form of composite specimens (fibre bundles embedded between two thin sheets of copper) stimulated by impact vs the single fibre – bending approach used for this research. Further tests that Bayramol carried out on the fibres were, determination of the tensile strength of the fibres (determination of tenacity), Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Scanning electron microscopy (SEM), and dynamic mechanical analysis (DMA).

The FTIR measurements were also carried out at the University of Bolton. The washing treatment of the samples and the measurements of the peak-to-peak voltage (V_{p-p}), were carried out in the Laboratories of the Department of Electronic Engineering at the Piraeus University of Applied Sciences. The measuring approach and a sampling of the results were presented at the 5th International Technical Textiles Congress, held in Izmir, Turkey, 7-9 November 2012 (Vassiliadis et al., 2012).

The characteristic dimensions of the yarns' cross sections produced through the process described below were for the ribbon yarns (a) PVDF yarn width 2.3 mm and thickness 0.11 mm, (b) PP yarn width 3.00 mm and thickness 0.09 mm, while the monofilament yarns had a diameter of (a) PP 0.32 mm, (b) PVDF 0.30 mm and (c) PA11 0.50 mm.

Based on the existing literature on the electromechanical response of melt-spun piezoelectric textile fibres – presented in detail in Chapter 2- the most commonly used methods for the determination of electrical response of the fibres is to measure the voltage produced after the fibres have been mechanically stimulated by tensile strain, impact, or compression. As there is no standardised method/ instrument the testing setup had to be designed and set up in the lab. A diagram of this set up is provided below, Figure 5.

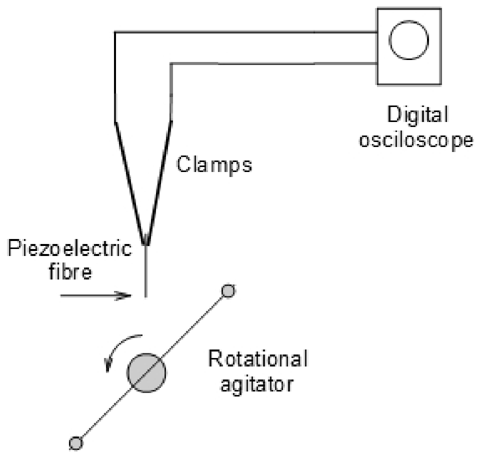


Figure 5. Diagram of the experimental set-up used for measuring the voltage produced by stimulation of piezoelectric fibres.

The piezoelectric fibres were clamped in a grip. The two plates of the grip were connected to the probe of an oscilloscope (Agilent DSO3202A Digital Storage Oscilloscope). The yarns themselves were stimulated using a rotating fin. The measurements took place under varying stimulation frequencies achieved by fixing the stimulating fin (rotational agitator) on the rotating shaft of a direct current (DC) motor. The correlation between the power voltage and rotating speed of the DC motor was proven to be linear, hence the different speeds of stimulation by the fin were expressed in arbitrary rotating speed units in the results. The typical electrical response ($V_{p\text{-}p}$) for the fibres can be seen in Figure 6. The image was captured by the oscilloscope and depicts clear well-defined peaks that correspond to stimulation and gradual dissipation phases upon contact with the rotating fin.

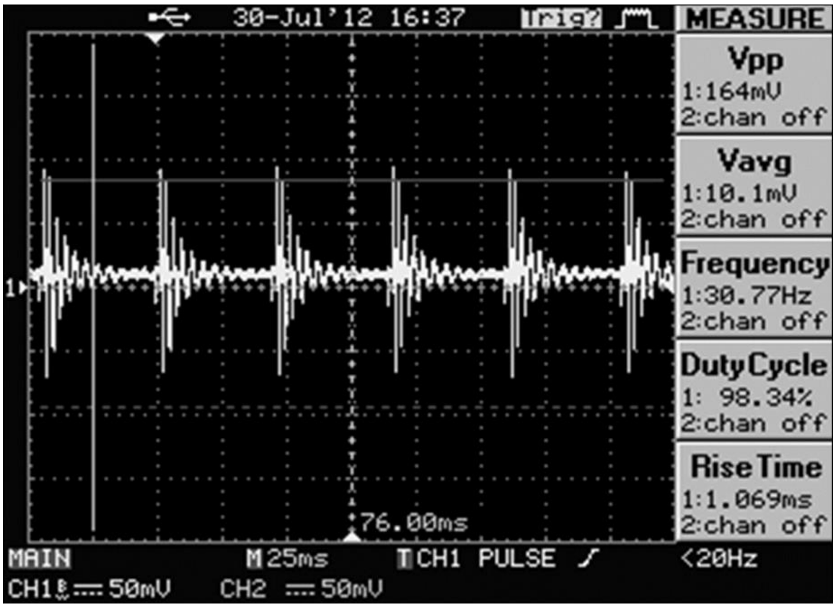


Figure 6. Typical voltage waveform produced during periodical stimulation

Regarding the washing procedure, chosen for the treatment of the samples, the choice was made based on the current standardised methods already existing for the testing of textile materials and specifically for washing of small specimens. The testing method (BS EN ISO 105-C06:2010) is commonly used for the determination of the colour fastness to washing at temperatures ranging from 40 ^{0}C to a maximum of 95^{0}C. To simulate more closely the mechanical action, that the materials undergo during washing, the method gives the option to use steel balls in the washing container together with the detergent solution. In the case of this research, the choice was made to not use the steel balls to prevent mechanical wear to the fibres.

The washing treatment was carried out at 40 ^{0}C according to test procedure A2S. The detergent used was ECE Reference Detergent for colour fastness testing, without optical brightener. Washing was carried out in an Ahiba IR dyeing machine, which is a standardized equipment used for the colour fastness to washing test.

The fibre specimens that were tested came in three different compositions and two different cross sections. Namely, the cross-sectional geometries examined were circular monofilament and flat ribbon and the compositions were polypropylene (PP), polyvinylidene difluoride (PVDF) and polyamide 11 (PA-11). PA-11 was only tested in monofilament cross-section as the fibre formation from PA11 polymer caused difficulties due to high moisture uptake behaviour.

3.2. Results - Discussion

As described in the paper the FTIR spectra of the fibres were determined in the pristine form of the fibres and then after washing procedure (Figure 8). For the PP yarns, no significant changes were observed in the spectra before and after washing. From the analysis of the spectra of the PA-11 yarn (pristine – washed) it was observed that, there was slight increase in the absorbance in the range of 800– 500 cm^{-1} which comprises the amide V and VI bands as well as a reduction in the intensity of the1635 cm^{-1} band that indicates that the well-known hydrogen-bonded b-sheet structure of polyamide-11 (Gao and Scheinbeim, 2000), this along with a reduction in the peak intensity of N–H band at 3300 cm^{-1} could be ascribed to the uptake of water by the polyamide (Nair et al., 2006).

For the PVDF samples, the differences in crystallinity (the relative fraction of piezoelectric β-phase) were calculated according to the method presented by Salimi and Yousefi (2003) (c.f. the attached copy of the paper). For PVDF monofilament yarns, this corresponds to a 70.86% of β-phase on the pristine (unwashed) sample, as compared to 56.59% of β-phase on the washed sample. For the ribbon yarns, the percentages are 54.29% (unwashed-pristine) and 48.76% (washed), respectively. It can be clearly observed that for the same drawing ratio, the PVDF monofilaments show the presence of higher β-phase as compared to the PVDF ribbons due to the higher thickness of the ribbons which manifests itself in the formation of lesser number of β-phase fibrils (Lund and Hagström, 2010; Soin et al., 2014).

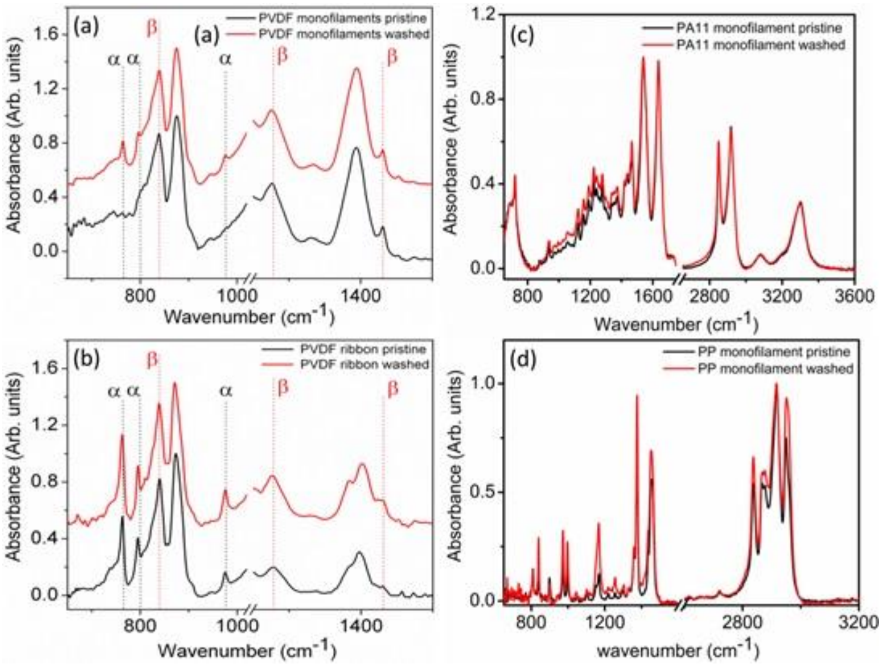
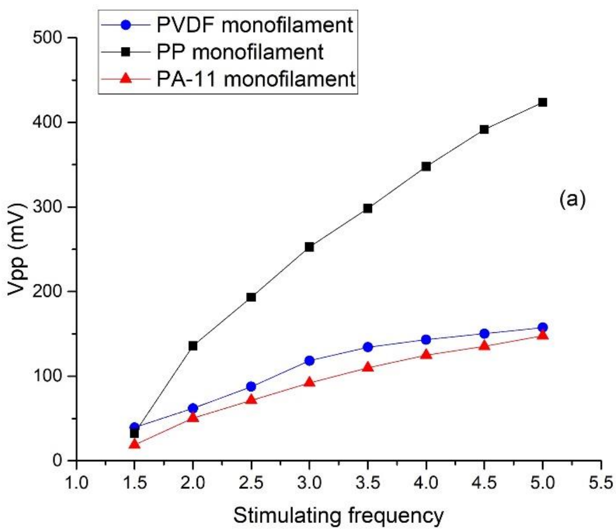


Figure 7. FTIR spectra of (a) PVDF monofilament, (b) PVDF ribbon yarn, (c) PA11 monofilament and (d) PP monofilament before

The maximum voltage response of the pristine samples (which for all fibre samples coincided with the response for the maximum stimulating frequency) was generally in the area of some hundreds mV, with the pristine PVDF ribbon yarn achieving the highest voltage at approximately 700mV. in contrast, the response of the pristine PVDF monofilament yarn was approximately 130mV. Hence it could be argued that the cross-section shape has indeed an effect on the voltage generation for the PVDF yarns. Obviously, the flat shape of the yarn is more suitable for maintaining clear the orientation of the piezoelectric structure. The round shapes have no means of indication of the potential piezoelectric orientation.

For the PP yarns, the monofilament yarn showed a distinctly higher response across all the simulating frequencies compared to the ribbon yarn. At the highest stimulation speed, PP monofilament yarn showed a Vpp 423 mV, while PP ribbon yarn showed a $V_{p\text{-}p}$ around 390 mV. The response of the PA-11 yarn which was only investigated in monofilament form, was the lowest of the responses observed in the monofilament samples (Figure 8).

The differences in the electrical responses between the fibres with different cross sections can be attributed to the different dimensions of the fibres as reported in paragraph 3.1. Namely to the differences in the cross-section areas of the yarns. i.e. PVDF ribbon yarn 0.253mm^2 vs PVDF monofilament 0.07065 mm^2. In the case of the PP ribbon yarn 0.27mm^2 vs PP monofilament 0.080384 mm^2. Also, as mentioned above the circular cross sections have no means of indication of the piezoelectric orientation which makes maintaining the same orientation between specimens difficult.



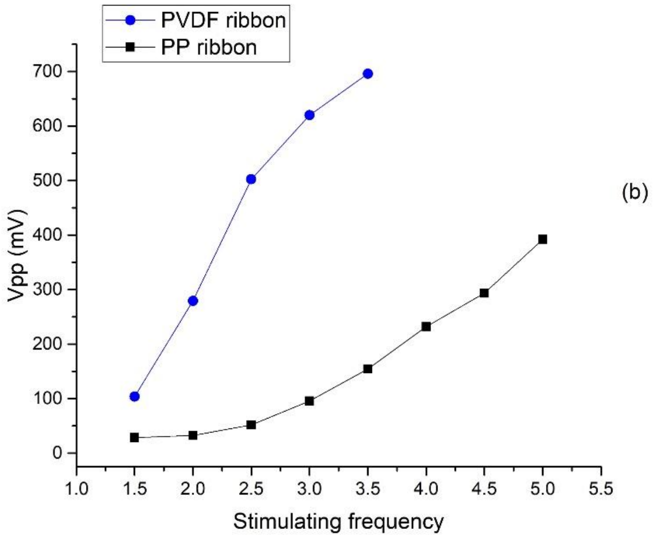
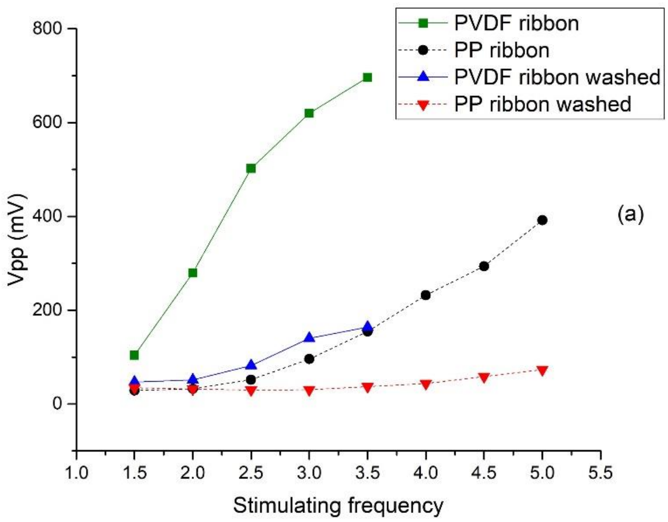


Figure 8. Peak-to-peak voltage generation of pristine (a) monofilaments and (b) ribbon yarns.

Comparing the electrical response of the fibres before and after washing it was observed that all the yarns in ribbon form showed a decrease in the voltage produced after one wash cycle (Figure 9a), while the yarns with a circular cross-section (monofilaments) showed an increase to the voltage produced, except for the PP monofilament yarn that did not show any significant alteration to the voltage produced between pristine and washed specimens (Figure 9b).

Regarding the piezoelectric PP ribbon yarn specimens, a dramatic decrease in V_{p-p} generation, was observed after the wash cycle. As seen in Figure 9a, the washed PP ribbon yarn showed a voltage generation of less than 100 mV_{p-p}, while the unwashed samples produced around 400 mV_{p-p} – values considered at the maximum stimulating frequency. The results for V_{p-p} measurements of PVDF yarn specimens show that the monofilament samples exhibit higher voltage after washing, whereas the ribbon yarn specimens exhibit lower V_{p-p}.

While the piezoelectric behaviour of PVDF has been investigated in detail since the observation of a large piezoelectric moment in oriented PVDF films by Kawai (Kawai, 1969), the review of the literature did not uncover any similar research that has been carried out on PP with regards to its piezoelectric behaviour in single film or fibre form. In contrast the piezoelectric behaviour of cellular PP has been widely investigated (c.f. Chapter 2). Further research, on additional specimens of the piezoelectric fibres, is required in order to determine the exact causes of the behaviour of the yarns, and especially in the case of the polypropylene yarns where the mechanism of piezoelectricity of single fibres is not precisely defined.



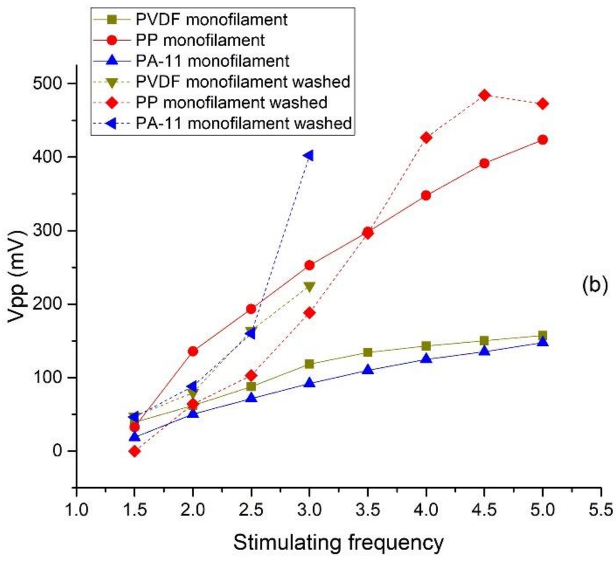


Figure 9. Peak-to-peak voltage generation of (a) ribbons and (b) monofilaments before and after washing

One of the points that became apparent during the research was the difficulty of maintaining the same orientation for all the samples in the case of monofilament yarns (circular cross section) since the circular cross sections have no means of indication of the potential piezoelectric orientation

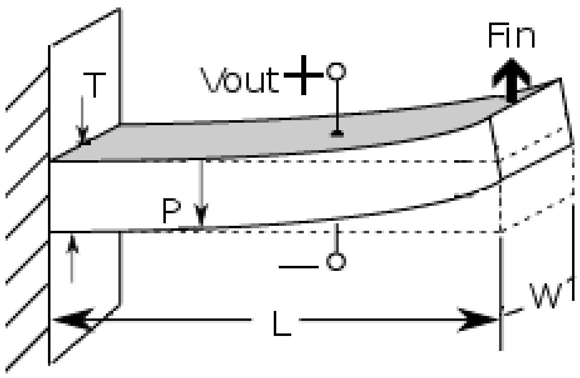


Figure 10. Bending mode diagram, L indicates the length of the piezoelectric fibre, W the width, T the thickness, P is the polarization, Fin is the bending force – including Voltage output indication.

As mentioned earlier polarisation of the textile fibres was carried out perpendicular to the longitudinal axis of the fibre i.e. in the direction of the z-axis (in other words subscript 3), assuming that the length of the fibre is the x-axis (subscript 1). The deformation of the fibre due to the mechanical stimulation is along the y-z plane (Figure 10).

Chapter 4 “On the Measurement of the Electrical Power Produced by Melt Spun Piezoelectric Textile Fibres”

“On the Measurement of the Electrical Power Produced by Melt Spun Piezoelectric Textile Fibres” (Matsouka et al., 2016b)(Appendix B) was published in June 2016 in the Journal of Electronic Materials (impact factor 1.579). The paper subject was the development of an innovative method/ apparatus for the measurement of the electrical power produced by melt-spun piezoelectric textile fibres. Construction of the apparatus was deemed necessary as, explained below, based in the current literature review, there was no standardized, efficient, and appropriate method for the characterisation of melt spun piezoelectric textile fibres with regards to the power produced.

4.1. Introduction

Reviewing the published literature on the determination of the electromechanical characteristics of piezoelectric, melt spun, textile fibres and specifically the electrical response of the fibres after mechanical stimulation (cf Chapter 2) germane to the energy harvesting behaviour of the fibres, it became evident that the previous attempts did not take into consideration the internal resistance of the material (i.e. considered the piezoelectric fibres as a power source). Stating the voltage produced during mechanical stimulation of the fibres is not enough to characterise the potential of the fibres as power sources (cf. voltage produced due to electrostatic phenomena on textiles where the voltage is in the range of several kV, but the power is not enough to power a light-emitting diode).

The theory connecting the internal resistance to the power output of a power source has been covered extensively in the relevant literature and it follows the maximum power transfer theorem (Suresh Kumar, 2009). The theorem states that the maximum amount of power will be dissipated in the load resistance if it is equal in value to the Thevenin or Norton source resistance of the network supplying the power. Graphically the relationship between power and load resistance is depicted in Figure 11, where it is shown that the Maximum Power Transfer occurs in the load when the load resistance is equal in value to the source resistance. This is called a “matched condition” and generally, maximum power is transferred from an active device such as a power supply or battery to an external device when the impedance of the external device exactly matches the impedance of the source. Hence in the cases of energy harvesting via piezoelectric fibres it is important to determine the power produced by the fibres when connected to a load (external resistance – closed circuit) to understand the true capabilities of the fibres.

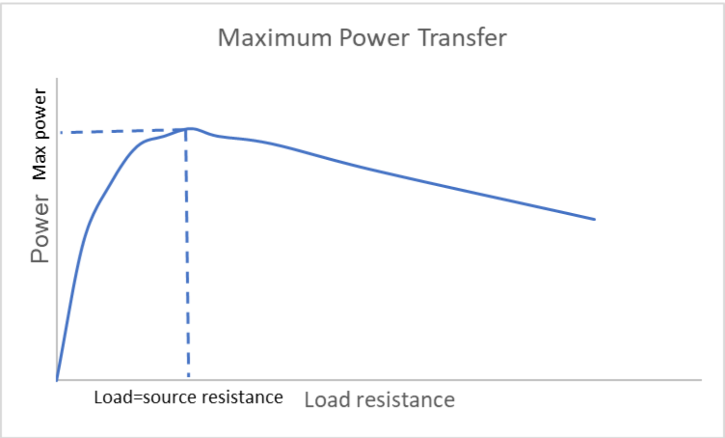


Figure 11. Maximum Power Transfer

4.2. Materials - Methods

The materials used for the research, PP, PA-11 and PVDF fibre samples, were provided by IMRI at the University of Bolton and came from the same batch of fibres produced by Bayramol (2012) as discussed in the previous chapter. The FTIR and DSC measurements were also carried out at the University of Bolton. The measurements of the power produced by the fibres was carried out in the Laboratories of the Department of Electronic Engineering at the Piraeus University of Applied Sciences. Design and construction of the measuring equipment was also carried out in the Laboratories of the Department of Electronic Engineering. The measuring approach and sampling of the results were presented at the XIII International Izmir Textile and Apparel Symposium, held in Izmir, Turkey, 2-5 April 2014 (Vassiliadis et al., 2014).

The FTIR and DSC measurements carried out on the fibres were done to characterized – identified the fibres and obtain information regarding the crystallinity of their structure. The weight of the research and the paper was centred around the development of the testing method/ apparatus.

The design challenges encountered included the shape/material of the sample grabs, the method of standardization of the application of stress on the material and the measurement of power itself. Two major reasons guided this process; the mechanical and the electrical nature of the materials and the related restrictions imposed. The diameter of a typical textile fibre starts from few micrometres. A precise clamping device has been designed and developed so that the two plates of it will be parallel with an accuracy within the range of a couple of micrometres. The textile fibre, placed between the plates of the clamping device and held by them, acted as a spacer between the two plates of the clamp, ensuring that no electrical short circuit is present.

The choice to position the fibre clamping system in a vertical position and not horizontally was made, so that the device would be able to accommodate fibres made of “soft” materials that would “droop” when positioned horizontally. In Figure 12 the yarn stimulation system can also be seen below the clamping system. The distance between the clamping system and the rotating stimulation system can be adjusted through use of a telescopic, two-part, arm that can also be seen in Figure 12.

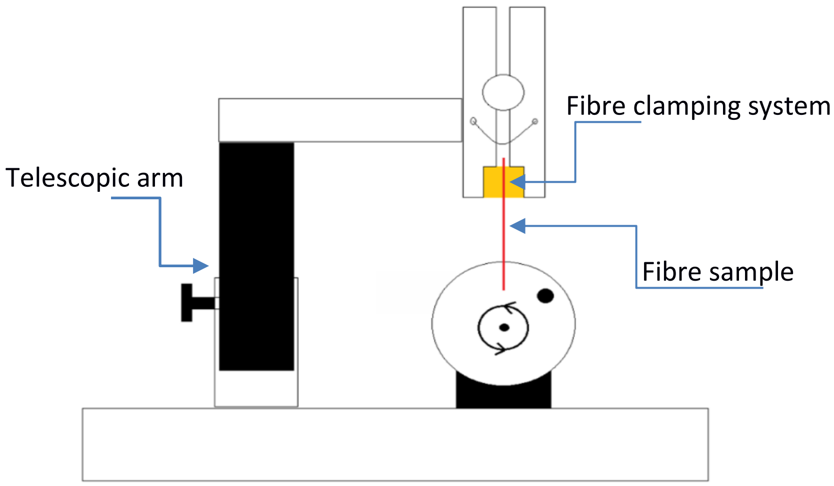


Figure 12. Schematic of the fibre clamping/ signal acquisition electrodes system mounted on the device.

The piezoelectric yarns are positioned and clamped in the grip. The grip simultaneously serves as a clamping device and as an electrode couple for the capturing of the electrical signal produced upon the mechanical stimulation of the fibres. The mechanical stimulation consists of a periodical deflection of the fibre and its immediate release. The free end of the fibre comes back to its neutral position ready for the next deformation cycle. The mechanical deformation of the fibre causes the generation of the piezoelectric power. Figure 13 shows the fibre clamping mechanism with an actual ribbon tape sample in place.

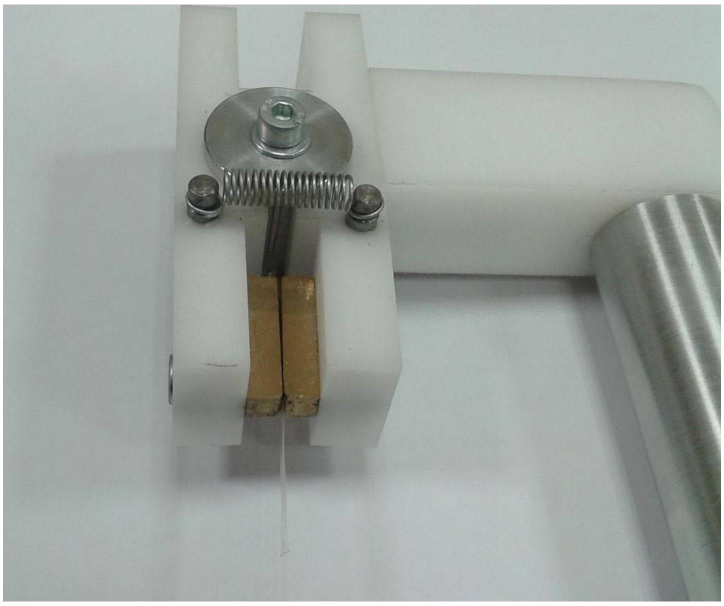


Figure 13. Fibre clamping system with piezoelectric ribbon yarn specimen inserted and secured in place

The fibre camping electrodes were constructed out of brass due to its high conductivity. During the experimentation in the design stage of the mechanical part of the device, copper and aluminium electrodes were also examined. Five different types of fibre clamping styles were examined, with the express desire to minimize the noise inserted in the measurement through the metallic elements of the clamps acting as antennae for the electromagnetic waves of the surrounding area - 50 Hz noise is a usual problem in electronics design (mains hum). In the end, it was decided to use a simple design for the clamps and to counter the noise through application of an electronic filter. An example of the reasons for discarding several electrode designs, in this case the triangular brass electrodes, were that the clamps damaged the fibres and that the fibres moved when the moving arm impacted it, due to the small area of contact between the fibre and the electrodes.

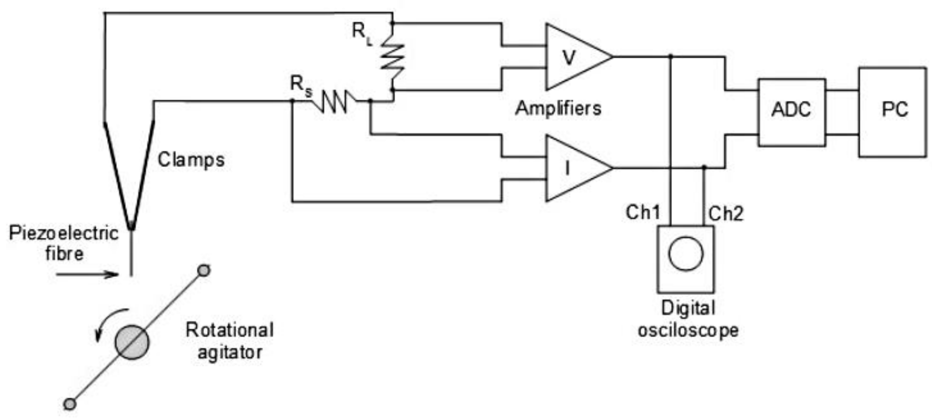
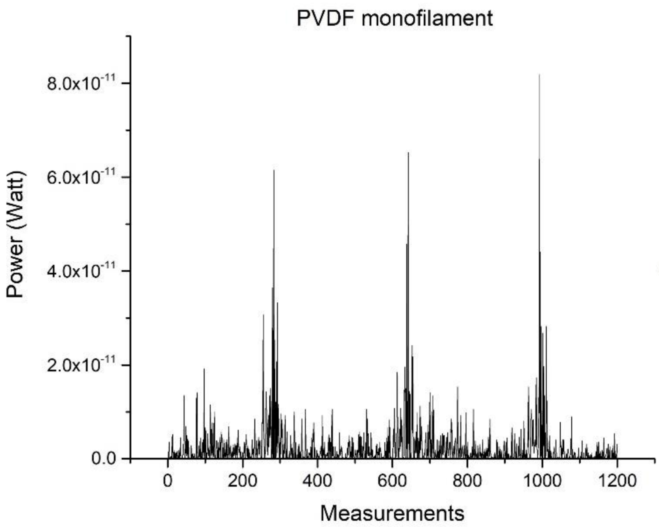


Figure *14*. Measurement principle

The electronic circuits of the test station were designed for capturing, amplifying, and conditioning of the signals before analogue to digital conversion. The digital signals are stored in a computer and are processed to receive the useful information and data related with the electrical behaviour and characteristics of the piezoelectric fibre. Figure 14 shows the measurement process with both the mechanical and electronic part in diagram form, with the shunt resistor (current measurement) and the load resistor (voltage measurement) clearly labelled. A typical sampling period is of 2ms. Since the phenomenon is clearly periodic there is no reason to store data from longer periods. The stored signals consist of approximately 1200 samples corresponding to about three stimulation intervals and three periods of the waveform as in Figure 15.

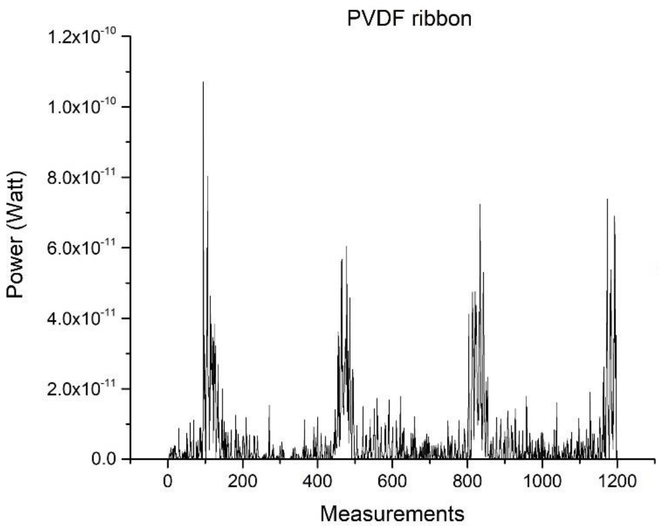
Furthermore, measuring both the voltage and the current generated by the specimens it became possible to discern the capacitive behaviour of the materials, a.k.a., the phase difference between voltage and current measurements.

4.3. Results-Discussion



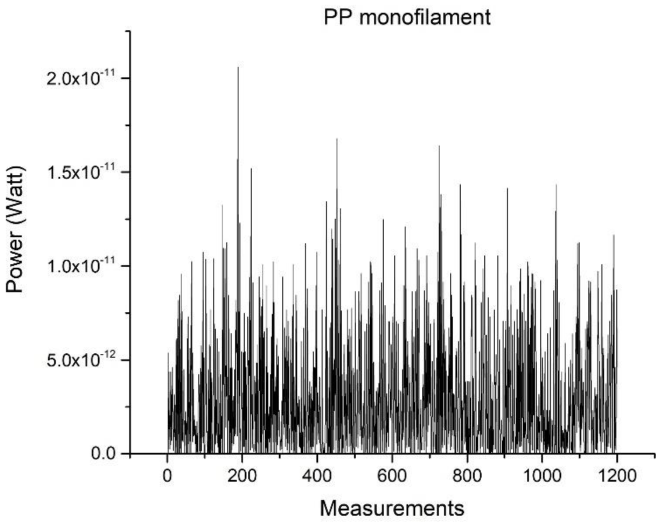
PVDF monofilament
Power (Watt)
Measurements

(a)

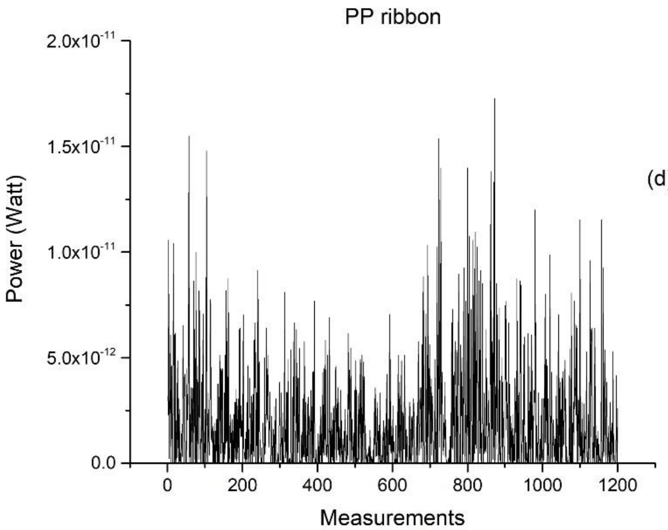


PVDF ribbon
Power (Watt)
Measurements

(b)


PP monofilament
Power (Watt)
2.0x10^-11
1.5x10^-11
1.0x10^-11
5.0x10^-12
0.0
0
200
400
600
800
1000
1200
Measurements

(c)


PP ribbon
Power (Watt)
2.0x10^-11
1.5x10^-11
1.0x10^-11
5.0x10^-12
0.0
0
200
400
600
800
1000
1200
Measurements

(d)

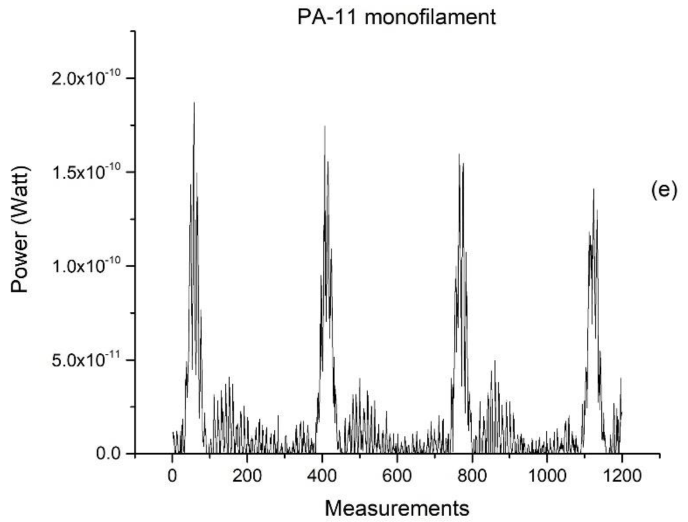


Figure 15. Power in Watts obtained from the yarns at 10 mm test length. (a) PVDF monofilament yarn, (b) PVDF ribbon yarn, (c) PP monofilament, (d) PP ribbon yarn, (e) PA-11 monofilament yarn.

A typical value of the power generated is of the order of nanowatts. For the total time of the three periods, the energy generated is in the range of picoJoules. The values of power and energy are small, but it must be considered that they correspond to a single fibre. In the textile structure of a cloth, thousands or even millions of fibres are engaged. In that sense, the total values of the power and energy are expected to be many orders of magnitude higher so that the electrical power produced will be considerable and useful for many applications, such as the operation of wearable or small electrical equipment or charging of batteries or capacitors.

Tests were carried out on specimens of different lengths ranging from 10mm to 20mm. The results showed that the power generated by the yarns was not connected with the distance between the grab point and the point of impact (Table 6).

These results agree with the findings of Vossou et al (2013) who carried out a computational investigation of the mechanical behaviour of the fibres, using the results from the measurements of V_{p-p} of the pristine fibres (Vassiliadis et al., 2012). Modal analysis of a piezoelectric fibre was performed with the use of the finite elements method in order to evaluate its eigenfrequencies and mode shapes. Based on the results of the research it was suggested that the production of electric power through the stimulation of the fibres is confined to the clamped area of the fibre i.e. the specific area of the fibre that is being bended.

Table 6. Power measurement results for the samples at different test lengths

	Power (nW)		
	Sample/test length (mm)		
	10	15	20
PVDF monofilament (mm)	2.79	2.66	2.26
PVDF ribbon (mm)	3.88	3.66	3.88
PA-11 monofilament (mm)	4.93	2.96	3.57
PP monofilament (mm)	3.13	2.91	3.44
PP ribbon (mm)	3.03	2.98	2.27

In Figure 16 below photos of the testing equipment, developed for the measurement of power generated by piezoelectric fibres, can be seen.

Figure 16. Testing apparatus developed for the measurement of the electrical power produced by the piezoelectric fibres

Chapter 5 “Three-dimensional weft-knitted textile fabrics based capacitors”

“Three-dimensional weft-knitted textile fabrics based capacitors” (Matsouka et al., 2017a) (Appendix C) was published in May 2017 in the Journal of the Textile Institute (impact factor 1.128). The paper subject was the investigation and modelling of the capacitive behaviour of specially constructed three-dimensional weft-knitted fabrics.

5.1. Materials - Methods

The materials used for the research were three-dimensional, weft-knitted fabrics with variation in the composition and thickness and were provided by IMRI of the University of Bolton. The measurement of the capacitance of the specimens was carried out in the Laboratories in the Department of Electronic Engineering at the Piraeus University of Applied Sciences. The measuring approach and a sampling of the results were presented at the 7th World Conference in 3D fabrics and their Applications, held in Roubaix, France, 8-9 September 2016 (Matsouka et al., 2016a).

The needle notation for the basic structure of the fabrics can be seen in Figure 17. All the samples were constructed in a similar way. For the sample with the added elastane (Sample 4), the elastane was fed together with A&B yarns.

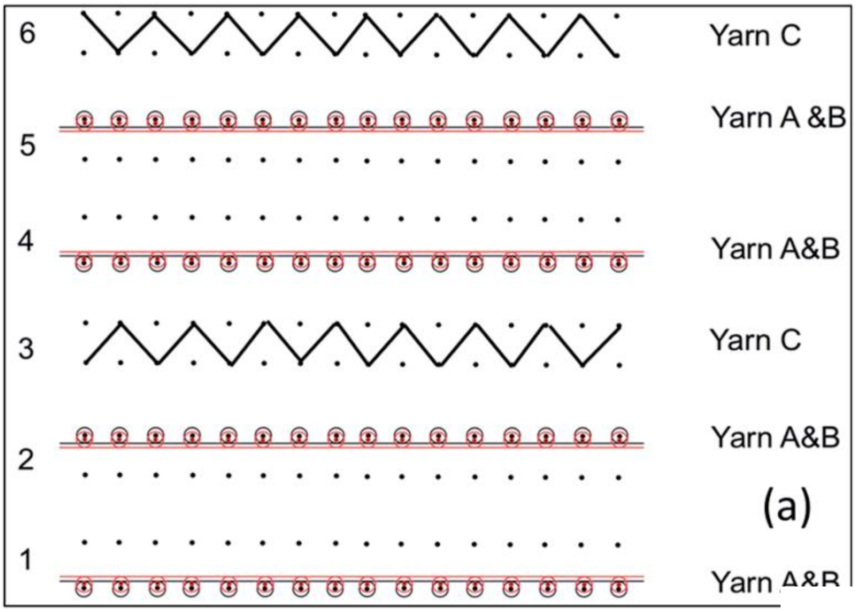


Figure 17. Needle notation for the structure of the 3D fabric samples – yarn A is the conductive yarn, yarn B is the insulating yarn and yarn C is the interconnecting monofilament yarn.

The specific description of the samples (Figure 18) is as follows:

- Sample No 1, outer layer knitted only with conductive yarn, interconnecting yarn PVDF, thickness 2.5mm
- Sample No 2, outer layer containing both the conductive and the insulating yarn, interconnecting yarn ZnSnO3-PVDF, thickness 2.5mm
- Sample No 3, outer layer containing both the conductive and the insulating yarn, interconnecting yarn PVDF, thickness 2.5mm and
- Sample No 4, outer layer containing the conductive yarn, the insulating yarn and elastane, interconnecting yarn PVDF, thickness 1.5mm

Soin et al. (2014) published a paper where the electrical response of a 3D spacer fabric, incorporating piezoelectric PVDF monofilament yarns as interconnecting material, was investigated concerning power generation. The fabric showed an output power density in the range of 1.10–5.10mWcm^{-2} at applied impact pressures in the range of 0.02–0.10MPa. Tests were carried out using a 3D spacer fabric similar to sample No 3 mentioned above.

Samples 1 to 4 represent variations to the structure of the 3D spacer fabric with regards to fabric composition and in the case of Sample 4 the thickness as well. While in the research by Soin et al, the point of the research was aimed at the investigation of the power production of the fabric, the research carried out in the Department of Electronic Engineering and published in the paper (Matsouka et al., 2017a) was aimed at investigating the electric properties of the fabrics and specifically their inherent capacitive behavior.

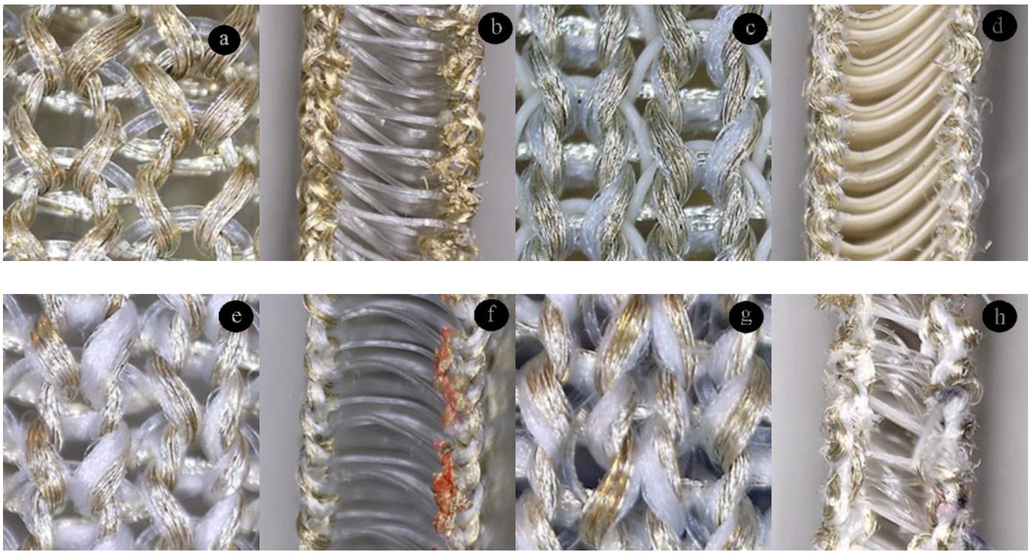


Figure 18. 3D Spacer fabrics; (a), (b) Sample 1 outer layer and thickness view, respectively, (c), (d) Sample 2, (e), (f) Sample 3 and, (g), (h) Sample 4.

A capacitor is a device consisting of two electrical conductors separated by a dielectric material (which as described in Chapter 2 is the overall group of materials that piezoelectrics are a subgroup). Theoretically, one could use any two conducting materials separated by an insulating material and construct a capacitor. Practically and depending on the application there are other factors that are involved, starting with the structural stability of the capacitor (lateral movement) and expanding to considerations regarding hysteresis and signal drift.

The 3D knitted structure addresses both these due to the inherent significant thickness along the z-axis, compared with traditional fabrics, woven, or knitted. Furthermore, 3D weft-knitted fabrics can be produced using a circular, double jersey machine which is a common type of knitting machine that is used to produce conventional knitting structures, allowing for utilization of existing equipment without the need for modifications. More importantly, the inclusion of the conductive element in the fabric construction removes the need for extraneous and additional steps described in the existing literature such as gluing; heat setting or sewing the parts of the capacitor.

The capacitive behavior of the samples was modelled based on the constituent equations describing the behaviour of capacitors and information about 3D fabric structure. The theoretical capacitance of a parallel plate capacitor is described by Equation (1). The equation correlates the capacitance with the geometric dimensions of the capacitor and the nature of the material between the plates. (ε_r and ε_o denote the relative static permittivity of the material between the plates and the permittivity of vacuum respectively).

$$C = \frac{\varepsilon_r \varepsilon_o A}{d} \quad (1)$$

Where,

C is the capacitance in Farad,

A is the area of overlap of the two plates in m^2, d is the separation distance of the two plates in m,

ε_r is the relative static permittivity (dielectric constant) of the material between the capacitor plates and

ε_0 is the electric constant or vacuum permittivity (approx. 8.854×10^{-12} F·m^{-1})

The values for the area and distance of the plates can be measured using fundamental methods; in the case of this project, the plate dimensions and the distance between them were obtained from images acquired through a stereoscopic microscope.

In order to calculate the equivalent relative static permittivity, the percentage of the volume between the capacitor plates occupied by the isolating filaments between the two conductive plates must be estimated. The volume occupied by the filaments was calculated in relation to the overall volume between the plates. Considering the space between the plates as a rectangular cuboid of the volume can be calculated using Equation (2).

$$V = dA \qquad (2)$$

Where,

V is the volume of the space between the capacitor plates in m^3,

d is the separation distance of the two plates in m and

A is the area of overlap of the two plates in m^2

The interconnecting monofilament yarns used in the production of the fabric samples have a circular cross section. Hence the filaments can be described as cylinders with an overall volume given by Equation (3).

$$V_f = nL\pi\left(\frac{D}{2}\right)^2 \qquad (3)$$

Where,

V_f is the overall volume of the filaments in m^3

n is the total number of filaments in the space between the plates, for the plates dimensions under consideration,

D is the diameter of the filaments in m and,

L is the actual length of the filaments in m. Note that L > d due to the filament curvature as can be seen in the stereoscopic microscope images (Figure 19).

The relative static permittivity of the mixture of air and filaments between the plates can be expressed as follows,

$$\varepsilon_r = \frac{\varepsilon_{rf}V_f+\varepsilon_{rV}(V-V_f)}{V} = \frac{V_f}{V}\left(\varepsilon_{rf} - \varepsilon_{rV}\right) + \varepsilon_{rV} \qquad (4)$$

Where,

ε_{rf} is the relative static permittivity of the interconnecting filament fibers, with a typical value of 9 F·m^{-1} for the PVDF material (Huang et al., 2009),

ε_{rv} is the relative static permittivity of the air, with a typical value of 1 F·m^{-1}

By replacing Equations (2), (3) and (4) into Equation (1) the following expression for the theoretical capacitance is derived (Equation (5).

$$C = \frac{\varepsilon_0 A}{d}\left[\frac{V_f}{V}\left(\varepsilon_{rf} - 1\right) + 1\right] \qquad (5)$$

Where,

C is the capacitance in Farad,

A is the area of overlap of the two plates in m^2,

d is the separation distance of the two plates in m,

V is the volume of the space between the capacitor plates in m^3,

V_f is the overall volume of the filaments occupying the space between the capacitor plates in m^3,

ε_{rf} is the relative static permittivity (dielectric constant) of the material of the interconnecting fibres with a typical value of 9 F·m^{-1} for the PVDF material

ε_0 is the electric constant or vacuum permittivity (approx. 8.854×10^{-12} $F{\cdot}m^{-1}$)

5.2. Results-Discussion

Testing was carried out using specimens of four different nominal areas, namely 1, 4, 9 and 16 cm^2. Specimen capacitance was measured using a Wayne Kerr Impedance Analyser 6500B series. Capacitance measurements were obtained for the frequency range from 100Hz to 10MHz. The individual results for the samples per area size can be seen in Figure 19. The measured capacitive behaviour of the samples vs the behaviour predicted by the calculations based on the model, per specimen area, at 5 and 10 MHz can be seen in Figure 20, while the results are presented in Tables 7 and 8 and the calculated capacitance can be seen in Table 9.

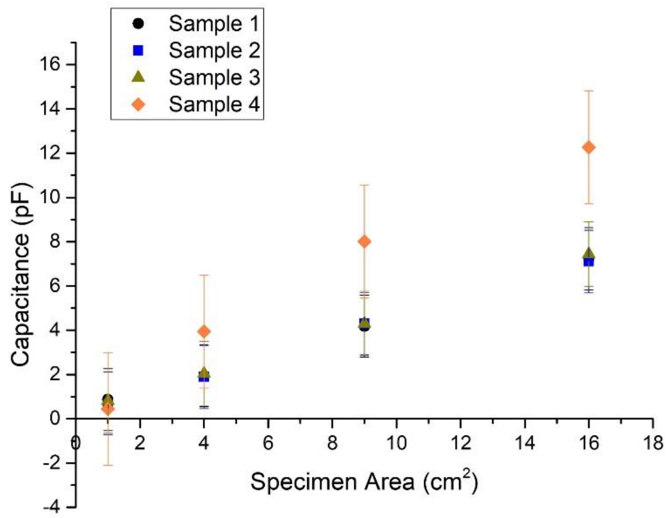


Figure 19. Measured capacitance per specimen area Samples 1, 2, 3 and 4. N.B the negative values of the capacitance depicted here and in Figure 18 are due to the use of the error bars and have no physical meaning.

Comparing the measured capacitance of Samples 1–3 (Figure 19 and Table 7), there is no significant difference between the values obtained for each of the samples. The addition of the insulating yarn and/or the different composition of the interconnecting monofilament (PVDF vs. ZnSnO3-PVDF) does not seem to influence the value of the capacitance. On the other hand, Sample 4 which is thinner than all the other samples (thickness of 1.5 mm compared to 2.5 mm) shows a distinctly different behaviour with capacitance values that are distinctly higher than those of the other three samples, for all specimen areas; except for the 1X1 cm^2 specimens where the very small dimensions of the specimen could have affected the accuracy of the measurement, with regards to the parallelism of the capacitor plates.

Table 7. Capacitance measurements at 10MHz

	Capacitance (pF)			
	Specimen Area (cm^2)			
	1	4	9	16
Sample 1	0.87	1.94	4.18	7.23
Sample 2	0.70	1.89	4.30	7.10
Sample 3	0.80	2.04	4.30	7.44
Sample4	0.44	3.95	8.01	12.27

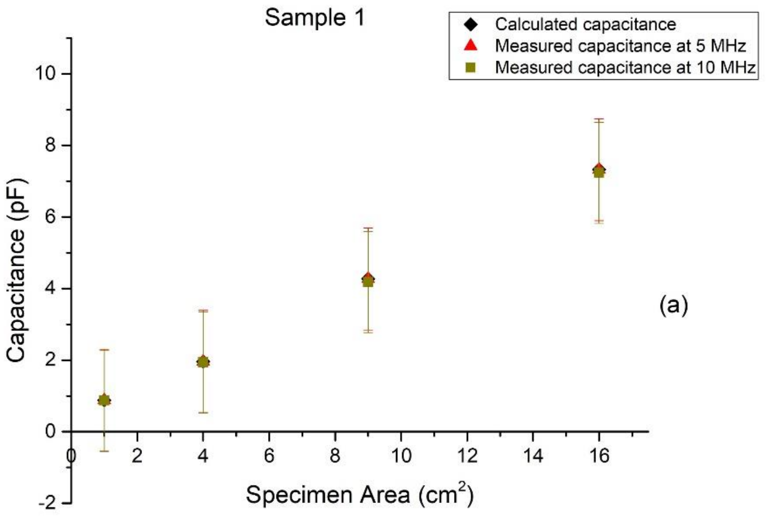
Table 8. Capacitance measurements at 5MHz

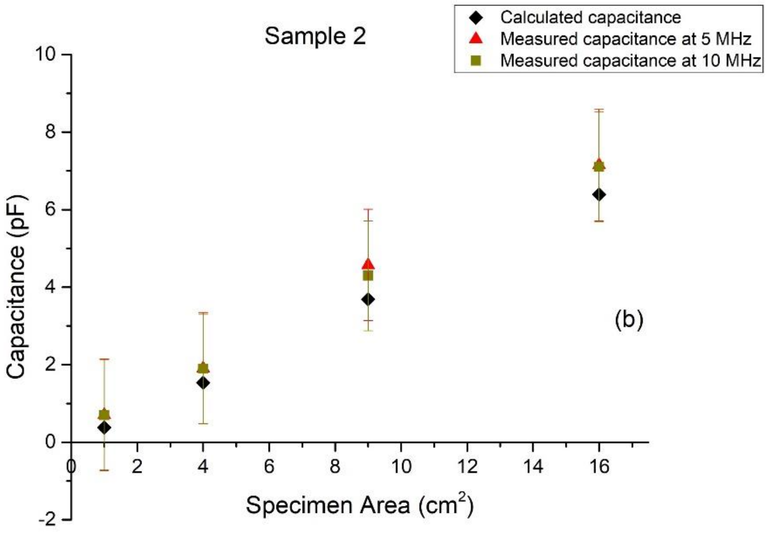
	Capacitance (pF)			
	Specimen Area (cm^2)			
	1	4	9	16
Sample 1	0.88	1.96	4.27	7.32
Sample 2	0.71	1.91	4.57	7.15
Sample 3	0.81	2.05	4.33	7.49
Sample4	0.31	3.99	8.07	12.36

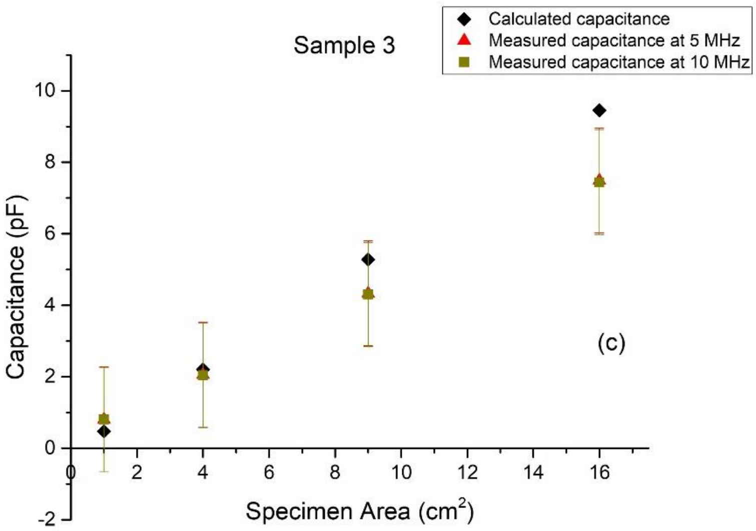
Table 9. Calculated capacitance

	Capacitance (pF)			
	Specimen Area (cm²)			
	1	4	9	16
Sample 1	0.69	2.30	5.36	9.70
Sample 2	0.38	1.53	3.68	6.39
Sample 3	0.47	2.20	5.28	9.45
Sample4	0.74	2.66	6.42	10.41

It should be noted that while Sample 4 has also elastane yarn knitted in the outer layers, this yarn is restricted to the outer layers and is not knitted in the space with the interconnecting yarns, hence it is not expected to alter the dielectric constant between the textile capacitor 'plates'. The ratio between the capacitance measurements for Sample 4 follows the expected ratio calculated based on the thicknesses.




Sample 2
Calculated capacitance
Measured capacitance at 5 MHz
Measured capacitance at 10 MHz
Capacitance (pF)
Specimen Area (cm²)
(b)


Sample 3
Calculated capacitance
Measured capacitance at 5 MHz
Measured capacitance at 10 MHz
Capacitance (pF)
Specimen Area (cm²)
(c)

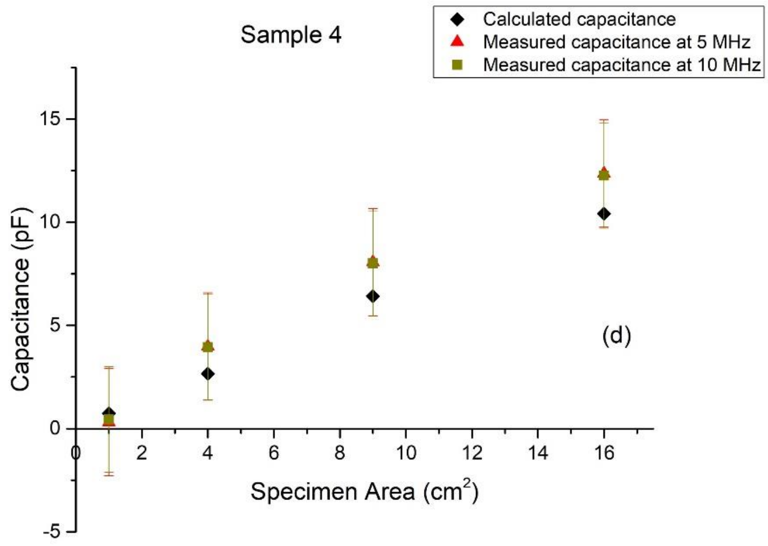


Figure 20. Measured capacitance vs. Calculated capacitance at 10 and 5 MHz (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4.

A significant finding was observed during the resonance testing of an LC (inductor–capacitor) textile circuit – which could be suitable for the implementation of resonant circuits that are convenient for basic electronic applications (i.e. oscillators, filters, etc.). As can be seen in Figure 22, which presents the imaginary part Xs (Ω) and the real (ohmic) part Rs (Ω) of the parallel combination of coil and capacitor against the testing frequency, the circuit achieved resonance at approximately 21 MHz, where the real part Rs reaches its maximum value (i.e. ~2500Ω).

Figure 21. Flat spiral coil embroidered on fabric (embroidered with stainless steel yarn and polyester yarn on polyamide substrate)

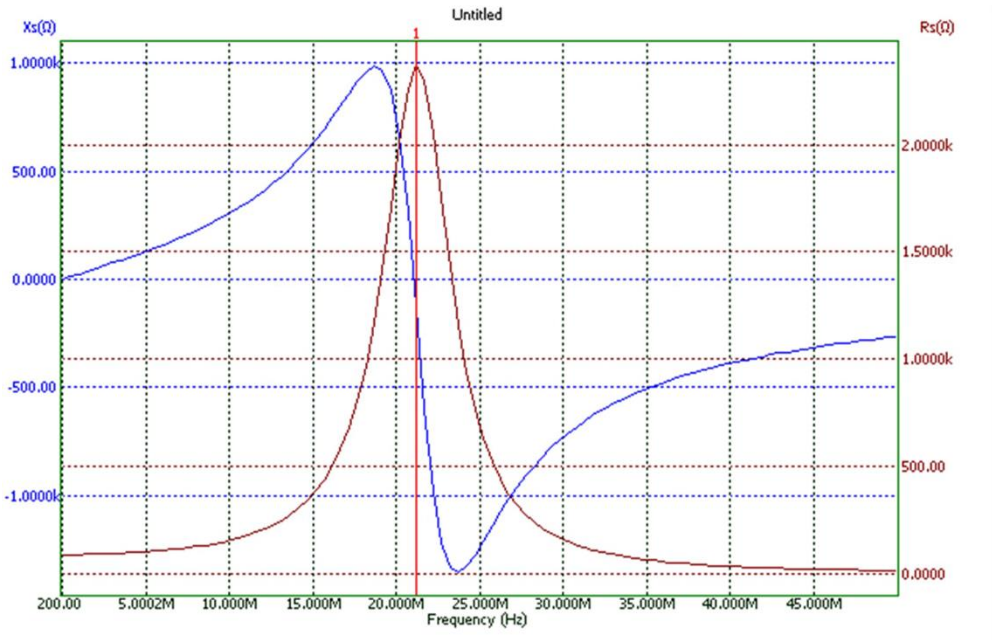


Figure 22. Resonance measurement of a textile-based parallel LC (inductor–capacitor) circuit.

While the research by Soin et al (Soin et al., 2014) demonstrated that this particular fabric structure and composition is a viable energy production material, this research highlighted that these 3D spacer fabrics showed a complementary characteristic of being suitable as capacitors in terms of measured capacitance and behaviour during compression.

This expands the functionality profile of these materials and allows for a wider range of possible applications when these materials are incorporated into textile structures. Moreover, the ability to achieve resonance between a textile-based capacitor and a similarly textile based induction coil, is very promising as well allowing for the possibility of creating fully textile signal filters or similar applications. In other words, these materials can be manufactured in one step, with existing methods and can behave as fully customizable capacitors.

Chapter 6 Discussions - Conclusions and Future work

The goal of this PhD research project by publication was to investigate the efficiency and durability of wearable smart materials and structures. To this end a set of objectives were defined. These objectives were:

- investigate the effect of the washing procedure on the electrical response of the fibres
- identify and investigate the methods that are used for the determination of the efficiency of piezoelectric melt-spun fibres
- develop a method/ apparatus to classify the fibres regarding their efficiency in the production of electric power
- investigate and model the capacitive behaviour of 3D weft knitted fabrics incorporating the piezoelectric melt-spun fibres.

To achieve these objectives two approaches were followed. One concerned the review of the published literature and the other designing suitable experimental setups in order to directly investigate the properties of the materials under examination.

The review of the relevant published literature was carried out by investigating literature concerning melt-spun piezoelectric textile fibres (production methods, properties and behaviour) as well as the materials used for the production of said fibres (PVDF, PP, PA-11). Also, the review included research into energy harvesting applications and the use and integration of textiles based electronic elements into textiles substrates with a direct connection to smart textiles applications. The detailed results of literature review can be found in Chapter 2.

While the area of melt-spun piezoelectric fibres is relevantly new (especially compared with the volume of research into piezoceramics), there exist two patents for the production of said fibres. One is concerned with the production of fibres in pure polymer form and the other with the production of core-spun fibres (Hagström et al., 2014; Siores et al., 2010).

Regarding the piezoelectric properties of materials used for the production of the fibres it was noted that the published research was focussed around the investigation of the behaviour of PVDF and several of its copolymers. Moreover, the nature of the piezoelectric behaviour of PVDF had be exhaustively investigated and the relationship of the crystalline β-phase to piezoelectricity well established. The volume of literature available regarding PA-11 a fellow polar polymer was not as expansive but the work by Newman (1990, 1980) remains seminal and relevant. Regarding the piezoelectric behaviour of PP, a significant body of work exists concerning the cellular piezoelectric structures of PP, while research in the mechanism of piezoelectricity for single layer PP films or fibre form is scarce.

Moreover, looking into the research published about the properties of the melt-spun fibres it was found that there was no research concerned with the effects of washing/ care treatments on the piezoelectric textile fibres, while the majority of the research was concerned with the characterization of the crystallinity of the fibres as a measure of the effectiveness of the production processes described in the research papers (as mentioned previously the piezoelectric properties of PVDF are connected to the presence of the β-phase).

Regarding the determination of the electrical response of the fibres the results of the literature review showed that all the research published on this subject made use of the voltage produced by the fibres during mechanical stimulation in open-circuit conditions (i.e. without a load).

Finally, the review of papers into the use and integration of textiles based electronic elements into textiles substrates, showed that there have been a number of attempts to construct textile based electronic elements, and specifically textile-based capacitors. These attempts involved discrete steps for the assembly of the capacitors and described structures that lacked the ability for easy customization and presented problems with structural stability.

Regarding the investigation of the effect of the washing procedure on the electrical response of the piezoelectric fibres, the research concluded that for the fibres that were tested the cross-section shape had a significant effect on the electrical response of the fibres after one wash cycle. Specifically, ribbon yarns showed a decrease in the voltage produced while monofilament yarns (circular cross section) showed an increase. Furthermore, regarding the effect of the composition of the fibres, when comparing the ribbon yarns, it was shown that PVDF yarn had a higher electrical response than PP yarn both before and after the wash cycle.

For the monofilament yarns while before washing the highest response was observed on the PP yarn (which showed similar behavior before and after washing), after washing both the PVDF and the PA-11 yarn showed electrical responses comparable to the response of the PP monofilament. The maximum electrical responses for all the yarns examined were in the level of hundreds of mV; with the pristine PVDF ribbon having the highest response close to 700 mV.

The findings of the research, pertaining to this research objective, were published as a paper entitled, “Investigation of the durability and stability of piezoelectric textile fibres” in July 2016 in the Journal of Intelligent Material Systems and Structures.

Regarding the identification and investigation of the methods used for the determination of the efficiency of the piezoelectric melt spun fibres the following conclusions were reached, i) most of the research carried out focused on PVDF core spun fibres with very few exceptions, ii) the majority of the current research utilized test methods such as XRD, DSC and FTIR to characterise piezoelectric fibres and iii) there is no standardized method for the determination of the electrical response of the fibres to mechanical stimulation (neither as a method nor as equipment).

Relevant to the characterisation of the electromechanical response of the fibres, there seem to be two approaches a) testing that is intended to show the potential of the fibres, i.e. qualitative tests, and b) testing that measures the voltage produced by the fibres when the fibres (or multifilament yarns or fabrics incorporating said yarns) are mechanically stimulated either by tensile strain, impact, or compression.

Regarding the objective to design, develop and construct a device/ method to characterise the fibres regarding their efficiency in the production of electric power, the device/ method was developed and used to characterize the electrical response of piezoelectric melt spun fibres. Measurements were carried out in different fibre specimen length and the results indicated that the power production capabilities of the fibres at different lengths were similar, i.e. the power response was not connected to the distance of the clamping point from the point of impact (for the lengths examined)

The results of the research into the electrical power production capabilities of piezoelectric melt spun textile fibres were published in a paper entitled "On the Measurement of the Electrical Power Produced by Melt Spun Piezoelectric Textile Fibres" in June 2016 in the Journal of Electronic Materials.

Regarding the investigation/ modelling of the capacitive behaviour of 3D weft knitted fabrics incorporating the piezoelectric melt-spun fibres it was concluded that, three-dimensional weft knitted fabric incorporating piezoelectric melt spun fibres and having an overall structure described in chapter 5, showed promising capacitive behaviour which can be considered as an advantageous supplementary characteristic to the power generation ability of these fabrics.

Furthermore, 3D fabric structures, by their inherent dimensions and structural stability thereof can solve quite a few of the problems faced by the attempts in the fabrication of textile based capacitors as described in the literature. The capacitive behaviour of the samples investigated ranged in the picoFarad values, with the specimens measuring 4X4 cm^2, achieving results of 7 to 12pF. An additional significant finding of the research was that when connected in parallel with a textile based flat coil inductor (conductive thread flat coil embroidered on fabric), the resulting circuit was able to achieve resonance.

The results of the research into capacitive behaviour of 3D weft knitted fabrics incorporating the piezoelectric melt-spun fibres were published in a paper entitled “Three-dimensional weft-knitted textile fabrics based capacitors” in May 2017 in the Journal of the Textile Institute

6.1 Future work

Smart textile structures incorporating electrically active components (either innovative textile based or standard ones) are very much in demand across the board in current research. Whether they are active or passive systems, for military or medical use, communications etc. the need for textiles structures with an “added” functionality is in demand. Capable to provide this added functionality whether as sensors or energy harvesting power generators piezoelectric textile yarns can be significant materials.

This research project touched on some of the less thoroughly investigated research areas connected to the efficiency and durability of piezoelectric melt spun fibres and structures. Suggestions for future work are given below.

While the durability testing of the piezoelectric fibres was carried out regarding the effect of washing cycles, washing being the most common care/ cleaning method on textiles, there are other factors that affect textiles whether they are used in garment (wearable) applications or not. A good example is the effect of UV radiation (a component of the radiation emitted by the sun) on the piezoelectric properties of the fibres (in single form or incorporated into a fabric structure). The effect of UV radiation on polymers with regards to their colour, strength, brittleness, i.e. the aging effect and the resistance to the same is a subject of interest and has been extensively investigated. The piezoelectric properties of a fabric such as the 3D fabric studied here that is expected to be used in an application exposing it to sunlight can be adversely affected as well.

Another important point highlighted by the research carried out for this PhD project by publication was the need for further investigation into the mechanism of piezoelectric behaviour of PP single fibres. Published research has described the piezoelectric behaviour of cellular PP, while research into single fibre piezoelectricity is scarce.

Investigation of the applicability of the testing method developed in this research project, on piezoelectric fibres/ yarns of different types, other than the ones referred to herein. An interesting example are core spun piezoelectric yarns where the piezoelectric polymer forms the outer layer of the monofilament and the centre of the yarn contains conductive additives such as carbon nanotubes. While the device has been designed with piezoelectric melt spun fibres in mind it could be altered/ improved to test piezoelectric fibres produced via other spinning technologies e.g. electrospinning.

Regarding the capacitive behaviour of the three-dimensional piezoelectric fabric structures, the research was centred into modelling and investigating the behaviour of the materials as capacitors. Further work could be done to exploit this fabric characteristic in sensor applications both single (one fabric) and / or creating a pressure sensing matrix, that could offer positioning information as well as pressure readings.

Moreover, for the fabrics studied here, the space between the outer layers of the 3D fabric was occupied by a mixture of air and the interconnecting piezoelectric monofilament yarn. Capacitive behaviour is quite sensitive to the material between the plates of the capacitor, metal, or textile. Due to this fact, the textile based capacitor can possibly be used as humidity indicators.

References

Abramovich, H., 2016. Intelligent materials and structures, De Gruyter Graduate. De Gruyter, Berlin Boston.

Anton, S.R., Sodano, H.A., 2007. A review of power harvesting using piezoelectric materials (2003–2006). Smart Mater. Struct. 16, R1–R21. https://doi.org/10.1088/0964-1726/16/3/R01

Avloni, J., Lau, R., Ouyang, M., Florio, L., Henn, A.R., Sparavigna, A., 2008. Polypyrrole-coated Nonwovens for Electromagnetic Shielding. J. Ind. Text. 38, 55–68. https://doi.org/10.1177/1528083707087834

Balint, R., Cassidy, N.J., Cartmell, S.H., 2014. Conductive polymers: Towards a smart biomaterial for tissue engineering. Acta Biomater. 10, 2341–2353. https://doi.org/10.1016/j.actbio.2014.02.015

Bayramol, D.V., 2012. Development of hybrid smart material structures for energy regeneration and their use in wearable devices. University of Bolton, Bolton, UK.

Bayramol, D.V., Soin, N., Hadimani, R.L., Shah, T.H., Siores, E., 2015. Effect of Addition of Multiwalled Carbon Nanotubes on the Piezoelectric Properties of Polypropylene Filaments. J. Nanosci. Nanotechnol. 15, 7130–7135. https://doi.org/10.1166/jnn.2015.10530

Beeby, S.P., Tudor, M.J., Koukharenko, E., White, N.M., O'Donnell, T., Saha, C., Kulkarni, S., Roy, S., 2004. Micromachined silicon generator for harvesting power from vibrations.

Beeby, S.P., Tudor, M.J., White, N.M., 2006. Energy harvesting vibration sources for microsystems applications. Meas. Sci. Technol. 17, R175–R195. https://doi.org/10.1088/0957-0233/17/12/R01

Berlincourt, D., 1981. Piezoelectric ceramics: Characteristics and applications. J. Acoust. Soc. Am. 70, 1586–1595. https://doi.org/10.1121/1.387224

British Standard Textiles, 2010. Tests for colour fastness. Part C06: colour fastness to domestic and commercial laundering.

Chen, T., Cai, Z., Yang, Z., Li, L., Sun, X., Huang, T., Yu, A., Kia, H.G., Peng, H., 2011. Nitrogen-Doped Carbon Nanotube Composite Fiber with a Core-Sheath Structure for Novel Electrodes. Adv. Mater. 23, 4620–4625. https://doi.org/10.1002/adma.201102200

Cherenack, K., van Pieterson, L., 2012. Smart textiles: Challenges and opportunities. J. Appl. Phys. 112, 091301. https://doi.org/10.1063/1.4742728

Cook, J.G., Cook, J.G., 2005. Man-made fibres, 5. ed. ed, Handbook of textile fibres. Woodhead Publishing, Cambridge.

Curie, J., Curie, P., 1880. Développement, par pression, de l'électricité polaire dans les cristaux hémièdres à faces inclinées. Comptes Rendus 294–295.

Das, T.K., Prusty, S., 2012. Review on Conducting Polymers and Their Applications. Polym.-Plast. Technol. Eng. 51, 1487–1500. https://doi.org/10.1080/03602559.2012.710697

Davis, G.T., McKinney, J.E., Broadhurst, M.G., Roth, S.C., 1978. Electric-field-induced phase changes in poly(vinylidene fluoride). J. Appl. Phys. 49, 4998–5002. https://doi.org/10.1063/1.324446

Despesse, G., Jager, T., Jean-Jacques, C., Léger, J.-M., Vassilev, A., Basrour, S., Charlot, B., 2005. Fabrication and characterization of high damping electrostatic micro devices for vibration energy scavenging, in: Proc. Design, Test, Integration and Packaging of MEMS and MOEMS. pp. 386–390.

Eguchi, M., 1925. XX. On the permanent electret. Philos. Mag. Ser. 6 49, 178–192. https://doi.org/10.1080/14786442508634594

Eriksson, S., Berglin, L., Gunnarsson, E., Guo, L., Lindholm, H., Sandsjö, L., 2011. Three-dimensional multilayer fabric structures for interactive textiles, in: The Third Conference in 3D Textiles and Their Applications, Wohan, China, 20110420.

Ferreira, A., Costa, P., Carvalho, H., Nobrega, J.M., Sencadas, V., Lanceros-Mendez, S., 2011. Extrusion of poly(vinylidene fluoride) filaments: effect of the processing conditions and conductive inner core on the electroactive phase content and mechanical properties. J. Polym. Res. 18, 1653–1658. https://doi.org/10.1007/s10965-011-9570-1

Fukada, E., 1955. Piezoelectricity of Wood. J. Phys. Soc. Jpn. 10, 149–154. https://doi.org/10.1143/JPSJ.10.149

Fukada, E., Yasuda, I., 1957. On the Piezoelectric Effect of Bone. J. Phys. Soc. Jpn. 12, 1158–1162. https://doi.org/10.1143/JPSJ.12.1158

Gao, Q., Scheinbeim, J.I., 2000. Dipolar Intermolecular Interactions, Structural Development, and Electromechanical Properties in Ferroelectric Polymer Blends of Nylon-11 and Poly(vinylidene fluoride). Macromolecules 33, 7564–7572. https://doi.org/10.1021/ma000111i

Glauß, B., Bettermann, I., Steinmann, W., Walter, S., Seide, G., Gries, T., Roth, G., 2015. Production and functionalizing of bicomponent fibers based on PVDF. Chem. Fibers Int. 66, 70–72.

Glauß, B., Jux, M., Walter, S., Kubicka, M., Seide, G., Wierach, P., Gries, T., Roth, G., 2015. Poling Effects in Melt-Spun PVDF Bicomponent Fibres. Key Eng. Mater. 644, 110–114. https://doi.org/10.4028/www.scientific.net/KEM.644.110

Glauß, B., Steinmann, W., Walter, S., Beckers, M., Seide, G., Gries, T., Roth, G., 2013. Spinnability and Characteristics of Polyvinylidene Fluoride (PVDF)-based Bicomponent Fibers with a Carbon Nanotube (CNT) Modified Polypropylene Core for Piezoelectric Applications. Materials 6, 2642–2661. https://doi.org/10.3390/ma6072642

Glynne-Jones, P., Tudor, M.J., Beeby, S.P., White, N.M., 2004. An electromagnetic, vibration-powered generator for intelligent sensor systems. Sens. Actuators Phys., Selected Papers from Eurosensors XVI Prague, Czech Republic 110, 344–349. https://doi.org/10.1016/j.sna.2003.09.045

Gomes, J., Serrado Nunes, J., Sencadas, V., Lanceros-Mendez, S., 2010. Influence of the β-phase content and degree of crystallinity on the piezo- and ferroelectric properties of poly(vinylidene fluoride). Smart Mater. Struct. 19, 065010. https://doi.org/10.1088/0964-1726/19/6/065010

Guo, X., Huang, Y., Cai, X., Liu, C., Liu, P., 2016. Capacitive wearable tactile sensor based on smart textile substrate with carbon black /silicone rubber composite dielectric. Meas. Sci. Technol. 27, 045105. https://doi.org/10.1088/0957-0233/27/4/045105

Guo, Z., Nilsson, E., Rigdahl, M., Hagström, B., 2013. Melt spinning of PVDF fibers with enhanced β phase structure. J. Appl. Polym. Sci. 130, 2603–2609. https://doi.org/10.1002/app.39484

Hadimani, R.L., Bayramol, D.V., Sion, N., Shah, T., Qian, L., Shi, S., Siores, E., 2013. Continuous production of piezoelectric PVDF fibre for e-textile applications. Smart Mater. Struct. 22, 075017. https://doi.org/10.1088/0964-1726/22/7/075017

Hagström, B., LUND, A., Nilsson, E., Ab, S.I., 2014. Method of producing a piezoelectric and pyroelectric fiber.

Hamedi, M., Forchheimer, R., Inganäs, O., 2007. Towards woven logic from organic electronic fibres. Nat. Mater. 6, 357–362. https://doi.org/10.1038/nmat1884

Häsler, E., Stein, L., Harbauer, G., 1984. Implantable physiological power supply with PVDF film. Ferroelectrics 60, 277–282. https://doi.org/10.1080/00150198408017528

Hayakawa, R., Wada, Y., 1973. Piezoelectricity and related properties of polymer films, in: Fortschritte Der Hochpolymeren-Forschung, Advances in Polymer Science. Springer Berlin Heidelberg, pp. 1–55.

Heywang, W., Thomann, H., 1984. Tailoring of Piezoelectric Ceramics. Annu. Rev. Mater. Sci. 14, 27–47. https://doi.org/10.1146/annurev.ms.14.080184.000331

Hillenbrand, J., Sessler, G.M., 2000. Piezoelectricity in cellular electret films. IEEE Trans. Dielectr. Electr. Insul. 7, 537–542.

Holleczek, T., Rüegg, A., Harms, H., Tröster, G., 2010. Textile pressure sensors for sports applications, in: 2010 IEEE Sensors. Presented at the 2010 IEEE Sensors, pp. 732–737. https://doi.org/10.1109/ICSENS.2010.5690041

Huang, X., Jiang, P., Kim, C., Liu, F., Yin, Y., 2009. Influence of aspect ratio of carbon nanotubes on crystalline phases and dielectric properties of poly(vinylidene fluoride). Eur. Polym. J. 45, 377–386. https://doi.org/10.1016/j.eurpolymj.2008.11.018

Jang, S.-J., 2000. Ferroelectrics, in: John Wiley & Sons, Inc. (Ed.), Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc., Hoboken, NJ, USA. https://doi.org/10.1002/0471238961.0605181810011407.a01

Jean-Mistral, C., Basrour, S., Chaillout, J.-J., 2010. Comparison of electroactive polymers for energy scavenging applications. Smart Mater. Struct. 19, 085012. https://doi.org/10.1088/0964-1726/19/8/085012

Jost, K., Dion, G., Gogotsi, Y., 2014. Textile energy storage in perspective. J. Mater. Chem. A 2, 10776. https://doi.org/10.1039/c4ta00203b

Jukka Lekkala, Risto Poramo, Krister Nyholm, Timo Kaikkonen, 1996. EMF force sensor - a flexible and sensitive electret film for physiological applications. Med. Biol. Eng. Comput., The 1Oth Nordic-Baltic Conference on Biomedical Engineering, June g-13, 1996, Tampere, Finland 34, 67–68.

Kawai, H., 1969. The Piezoelectricity of Poly (vinylidene Fluoride). Jpn. J. Appl. Phys. 8, 975–976. https://doi.org/10.1143/JJAP.8.975

Kechiche, M.B., Bauer, F., Harzallah, O., Drean, J.-Y., 2013. Development of piezoelectric coaxial filament sensors P(VDF-TrFE)/copper for textile structure instrumentation. Sens. Actuators Phys. 204, 122–130. https://doi.org/10.1016/j.sna.2013.10.007

Khoffi, F., Khenoussi, N., Harzallah, O., Drean, J.Y., 2011. Mechanical behavior of polyethylene terephthalate/copper composite filament. Phys. Procedia 21, 240–245. https://doi.org/10.1016/j.phpro.2011.11.001

Klimiec, E., Królikowski, B., Machnik, M., Zaraska, W., Dzwonkowski, J., 2015. Increase of Piezoelectric Constant and Thermal Durability of Polypropylene Electret by Introducing SiO2 and Kaolin Filler and Creating a Cellular Structure. J. Electron. Mater. 44, 2283–2291. https://doi.org/10.1007/s11664-015-3719-3

Kravtsov, A.G., Brünig, H., Zhandarov, S.F., 2002. Analysis of the polarization state of melt-spun polypropylene fibers. J. Mater. Process. Technol. 124, 160–165. https://doi.org/10.1016/S0924-0136(02)00129-2

Kymissis, J., Kendall, C., Paradiso, J., Gershenfeld, N., 1998. Parasitic power harvesting in shoes, in: Wearable Computers, 1998. Digest of Papers. Second International Symposium On. IEEE, pp. 132–139.

Lee, C.S., Joo, J., Han, S., Koh, S.K., 2004. Multifunctional transducer using poly (vinylidene fluoride) active layerand highly conducting poly (3,4-

ethylenedioxythiophene) electrode: Actuator and generator. Appl. Phys. Lett. 85, 1841–1843. https://doi.org/10.1063/1.1784890

Lee, C.S., Joo, J., Han, S., Lee, J.H., Koh, S.K., 2005. Poly (vinylidene fluoride) transducers with highly conducting poly (3,4-ethylenedioxythiophene) electrodes. Synth. Met. 152, 49–52. https://doi.org/10.1016/j.synthmet.2005.07.116

Li, H., Lal, A., Blanchard, J., Henderson, D., 2002. Self-reciprocating radioisotope-powered cantilever. J. Appl. Phys. 92, 1122–1127. https://doi.org/10.1063/1.1479755

Li, H., Tian, C., Deng, Z.D., 2014. Energy harvesting from low frequency applications using piezoelectric materials. Appl. Phys. Rev. 1, 041301. https://doi.org/10.1063/1.4900845

Lund, A., Gustafsson, C., Bertilsson, H., Rychwalski, R.W., 2011. Enhancement of β phase crystals formation with the use of nanofillers in PVDF films and fibres. Compos. Sci. Technol. 71, 222–229. https://doi.org/10.1016/j.compscitech.2010.11.014

Lund, A., Hagström, B., 2011. Melt spinning of β-phase poly(vinylidene fluoride) yarns with and without a conductive core. J. Appl. Polym. Sci. 120, 1080–1089. https://doi.org/10.1002/app.33239

Lund, A., Hagström, B., 2010. Melt spinning of poly(vinylidene fluoride) fibers and the influence of spinning parameters on β-phase crystallinity. J. Appl. Polym. Sci. 116, 2685–2693. https://doi.org/10.1002/app.31789

Lund, A., Jonasson, C., Johansson, C., Haagensen, D., Hagström, B., 2012. Piezoelectric polymeric bicomponent fibers produced by melt spinning. J. Appl. Polym. Sci. 126, 490–500. https://doi.org/10.1002/app.36760

Ma, R., Lee, J., Choi, D., Moon, H., Baik, S., 2014. Knitted Fabrics Made from Highly Conductive Stretchable Fibers. Nano Lett. 14, 1944–1951. https://doi.org/10.1021/nl404801t

Magniez, K., Krajewski, A., Neuenhofer, M., Helmer, R., 2013. Effect of drawing on the molecular orientation and polymorphism of melt-spun polyvinylidene fluoride fibers: Toward the development of piezoelectric force sensors. J. Appl. Polym. Sci. 129, 2699–2706. https://doi.org/10.1002/app.39001

Małachowski, M., Żmija, J., 2010. Organic field-effect transistors. Opto-Electron. Rev. 18. https://doi.org/10.2478/s11772-010-0008-9

Martins, R.S., Gonçalves, R., Azevedo, T., Rocha, J.G., Nóbrega, J.M., Carvalho, H., Lanceros-Mendez, S., 2014. Piezoelectric coaxial filaments produced by coextrusion of poly(vinylidene fluoride) and electrically conductive inner and outer layers. J. Appl. Polym. Sci. 131, n/a-n/a. https://doi.org/10.1002/app.40710

Mateu, L., Moll, F., 2005. Optimum Piezoelectric Bending Beam Structures for Energy Harvesting using Shoe Inserts. J. Intell. Mater. Syst. Struct. 16, 835–845. https://doi.org/10.1177/1045389X05055280

Matsouka, D., Vassiliadis, S., Mytilinaios, S., Stathopoulos, N., Peres, Q., 2016a. 3d weft knitted textile fabrics based capacitors. Presented at the 7th World Conference in 3D fabrics and their Applications, Roubaix, France.

Matsouka, D., Vassiliadis, S., Mytilinaios, S., Stathopoulos, N., Siores, E., 2017a. Three-dimensional weft-knitted textile fabrics-based capacitors. J. Text. Inst. 1–8. https://doi.org/10.1080/00405000.2017.1330174

Matsouka, D., Vassiliadis, S., Prekas, K., Bayramol, D.V., Soin, N., Siores, E., 2016b. On the Measurement of the Electrical Power Produced by Melt Spun Piezoelectric Textile Fibres. J. Electron. Mater. 45, 5112–5126. https://doi.org/10.1007/s11664-016-4710-3

Matsouka, D., Vassiliadis, S., Vatansever Bayramol, D., Soin, N., Siores, E., 2017b. Investigation of the durability and stability of piezoelectric textile fibres. J. Intell. Mater. Syst. Struct. 28, 663–670. https://doi.org/10.1177/1045389X16657202

Meninger, S., Mur-Miranda, J.O., Amirtharajah, R., Chandrakasan, A., Lang, J.H., 2001. Vibration-to-electric energy conversion. IEEE Trans. Very Large Scale Integr. VLSI Syst. 9, 64–76.

Meyer, J., Arnrich, B., Schumm, J., Troster, G., 2010. Design and Modeling of a Textile Pressure Sensor for Sitting Posture Classification. IEEE Sens. J. 10, 1391–1398. https://doi.org/10.1109/JSEN.2009.2037330

Meyer, J., Lukowicz, P., Troster, G., 2006. Textile Pressure Sensor for Muscle Activity and Motion Detection. IEEE, pp. 69–72. https://doi.org/10.1109/ISWC.2006.286346

Mitcheson, P.D., Stark, B.H., Miao, P., Yeatman, E.M., Holmes, A.S., Green, T.C., 2003. Analysis and optimisation of MEMS electrostatic on-chip power supply for self-powering of slow-moving sensors, in: Proc. Eurosensors. pp. 492–495.

Mohammadi, B., Yousefi, A.A., Bellah, S.M., 2007. Effect of tensile strain rate and elongation on crystalline structure and piezoelectric properties of PVDF thin films. Polym. Test. 26, 42–50. https://doi.org/10.1016/j.polymertesting.2006.08.003

Murase, Y., Nagai, A., 1994. Melt spinning, in: Advanced Fiber Spinning Technology. Elsevier, pp. 25–64. https://doi.org/10.1533/9781845693213.25

Nair, S.S., Ramesh, C., Tashiro, K., 2006. Crystalline Phases in Nylon-11: Studies Using HTWAXS and HTFTIR. Macromolecules 39, 2841–2848. https://doi.org/10.1021/ma052597e

Neugschwandtner, G.S., Schwödiauer, R., Vieytes, M., Bauer-Gogonea, S., Bauer, S., Hillenbrand, J., Kressmann, R., Sessler, G.M., Paajanen, M., Lekkala, J., 2000. Large and broadband piezoelectricity in smart polymer-foam space-charge electrets. Appl. Phys. Lett. 77, 3827–3829. https://doi.org/10.1063/1.1331348

Newman, B.A., Chen, P., Pae, K.D., Scheinbeim, J.I., 1980. Piezoelectricity in nylon 11. J. Appl. Phys. 51, 5161–5164. https://doi.org/doi:10.1063/1.327283

Newman, B.A., Kim, K.G., Scheinbeim, J.I., 1990. Effect of water content on the piezoelectric properties of nylon 11 and nylon 7. J. Mater. Sci. 25, 1779–1783. https://doi.org/10.1007/BF01045384

Nilsson, E., Lund, A., Jonasson, C., Johansson, C., Hagström, B., 2013. Poling and characterization of piezoelectric polymer fibers for use in textile sensors. Sens. Actuators Phys. 201, 477–486. https://doi.org/10.1016/j.sna.2013.08.011

Nilsson, E., Mateu, L., Spies, P., Hagström, B., 2014. Energy Harvesting from Piezoelectric Textile Fibers. Procedia Eng. 87, 1569–1572. https://doi.org/10.1016/j.proeng.2014.11.600

Paajanen, M., Lekkala, J., Kirjavainen, K., 2000. ElectroMechanical Film (EMFi) — a new multipurpose electret material. Sens. Actuators Phys. 84, 95–102. https://doi.org/10.1016/S0924-4247(99)00269-1

Park, M., Im, J., Shin, M., Min, Y., Park, J., Cho, H., Park, S., Shim, M.-B., Jeon, S., Chung, D.-Y., Bae, J., Park, J., Jeong, U., Kim, K., 2012. Highly stretchable electric circuits from a composite material of silver nanoparticles and elastomeric fibres. Nat. Nanotechnol. 7, 803–809. https://doi.org/10.1038/nnano.2012.206

Park, S., Jayaraman, S., 2003. Smart Textiles: Wearable Electronic Systems. MRS Bull. 28, 585–591. https://doi.org/10.1557/mrs2003.170

Peltonen, J., Paajanen, M., Lekkala, J., 2000. Determination of the actuator sensitivity of electromechanical polypropylene films by atomic force microscopy. J. Appl. Phys. 88, 4789–4793. https://doi.org/10.1063/1.1290448

Perez-Rodriguez, A., Serre, C., Fondevilla, N., Cereceda, C., Morante, J.R., Esteve, J., Montserrat, J., 2005. Design of electromagnetic inertial generators for energy scavenging applications. Proc Eurosensors XIX Barc. Spain.

Potirakis, S., Jevsnik, S., Vassiliadis, S.G., Stathopoulos, N., Mytilinaios, S., 2017. Method of production of textile capacitors by hot welding (Metoda izdelave tekstilnih kondenzatorjev s toplim varjenjem). Slovenian Patent SI 25069.

Priya, S., Inman, D.J. (Eds.), 2009. Energy Harvesting Technologies. Springer US, Boston, MA.

Raju, M., Grazier, M., 2008. Energy Harvesting. Ti Com.

Ramadan, K.S., Sameoto, D., Evoy, S., 2014. A review of piezoelectric polymers as functional materials for electromechanical transducers. Smart Mater. Struct. 23, 033001. https://doi.org/10.1088/0964-1726/23/3/033001

Ramsay, M.J., Clark, W.W., 2001. Piezoelectric energy harvesting for bio MEMS applications, in: Proc. SPIE. pp. 429–438.

Roundy, S., Wright, P.K., 2004. A piezoelectric vibration based generator for wireless electronics. Smart Mater. Struct. 13, 1131. https://doi.org/10.1088/0964-1726/13/5/018

Rui, M., Marco, S., Renato, G., Gerardo, R., J.Miguel, N., Helder, C., Pedro, S., Senentxu, L.-M., 2014. Processing and Electrical Response of Fully Polymer Piezoelectric Filaments for E-Textiles Applications. J. Text. Eng. 60, 27–34. https://doi.org/10.4188/jte.60.27

Sajkiewicz, P., Wasiak, A., Gocłowski, Z., 1999. Phase transitions during stretching of poly(vinylidene fluoride). Eur. Polym. J. 35, 423–429. https://doi.org/10.1016/S0014-3057(98)00136-0

Salimi, A., Yousefi, A.A., 2003. Analysis Method. Polym. Test. 22, 699–704. https://doi.org/10.1016/S0142-9418(03)00003-5

Scheinbeim, J.I., Lee, J.W., Newman, B.A., 1992. Ferroelectric polarization mechanisms in nylon 11. Macromolecules 25, 3729–3732. https://doi.org/10.1021/ma00040a019

Sencadas, V., Gregorio, R., Lanceros-Méndez, S., 2009. α to β Phase Transformation and Microestructural Changes of PVDF Films Induced by Uniaxial Stretch. J. Macromol. Sci. Part B 48, 514–525. https://doi.org/10.1080/00222340902837527

Sergio, M., Manaresi, N., Tartagni, M., Guerrieri, R., Canegallo, R., 2002. A textile based capacitive pressure sensor. IEEE, pp. 1625–1630. https://doi.org/10.1109/ICSENS.2002.1037367

Sessler, G.M., Hillenbrand, J., 1999. Electromechanical response of cellular electret films. Appl. Phys. Lett. 75, 3405–3407. https://doi.org/10.1063/1.125308

Setter, N., Damjanovic, D., Eng, L., Fox, G., Gevorgian, S., Hong, S., Kingon, A., Kohlstedt, H., Park, N.Y., Stephenson, G.B., Stolitchnov, I., Taganstev, A.K., Taylor, D.V., Yamada, T., Streiffer, S., 2006. Ferroelectric thin films: Review of materials, properties, and applications. J. Appl. Phys. 100, 051606. https://doi.org/10.1063/1.2336999

Shad Roundy, 2005. On the Effectiveness of Vibration-based Energy Harvesting. J. Intell. Mater. Syst. Struct. 16, 809–823. https://doi.org/10.1177/1045389X05054042

Shenck, N.S., 1999. A demonstration of useful electric energy generation from piezoceramics in a shoe. Massachusetts Institute of Technology, Dept. of Electrical Engineering and Computer Science.

Shenck, N.S., Paradiso, J.A., 2001. Energy scavenging with shoe-mounted piezoelectrics. IEEE Micro 21, 30–42.

Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C.K., Heeger, A.J., 1977. Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH) x. J. Chem. Soc. Chem. Commun. 578. https://doi.org/10.1039/c39770000578

Silva, M.P., Martins, R.S., Carvalho, H., Nobrega, J.M., Lanceros-Mendez, S., 2013. Extrusion of poly(vinylidene fluoride) recycled filaments: Effect of the processing cycles on the degree of crystallinity and electroactive phase content. Polym. Test. 32, 1041–1044. https://doi.org/10.1016/j.polymertesting.2013.05.010

Siores, E., Hadimani, R.L., Vatansever, D., 2010. Piezoelectric Polymer Element & Production Method & Apparatus Therefor.

Siores, E., Vassiliadis, S.G., Matsouka, D., 2011. Energy harvesting and wearable electronics from the textile engineer's perspective. Presented at the eRA-6 International Scientific Conference, Athens, Greece.

Sobhani, H., Razavi-Nouri, M., Yousefi, A.A., 2007. Effect of flow history on poly(vinylidine fluoride) crystalline phase transformation. J. Appl. Polym. Sci. 104, 89–94. https://doi.org/10.1002/app.25519

Sohn, J.W., Choi, S.B., Lee, D.Y., 2005. An investigation on piezoelectric energy harvesting for MEMS power sources. Proc. Inst. Mech. Eng. Part C J. Mech. Eng. Sci. 219, 429–436. https://doi.org/10.1243/095440605X16947

Soin, N., Shah, T.H., Anand, S.C., Geng, J., Pornwannachai, W., Mandal, P., Reid, D., Sharma, S., Hadimani, R.L., Bayramol, D.V., Siores, E., 2014. Novel "3-D spacer" all fibre piezoelectric textiles for energy harvesting applications. Energy Environ. Sci. 7, 1670. https://doi.org/10.1039/c3ee43987a

Starner, T., Paradiso, J.A., 2004. Human generated power for mobile electronics, in: Low-Power Electronics Design. CRC Press.

Steingart, D., 2009. Power Sources for Wireless Sensor Networks, in: Energy Harvesting Technologies. Springer, Boston, MA, pp. 267–286. https://doi.org/10.1007/978-0-387-76464-1_9

Steinmann, W., Vad, T., Weise, B., Wulfhorst, J., Seide, G., Gries, T., Heidelmann, M., Weirich, T., 2013. Extrusion of CNT-modified Polymers With Low Viscosity - Influence of Crystallization and CNT Orientation on the Electrical Properties. Polym. Polym. Compos. 21, 473–482.

Steinmann, W., Walter, S., Seide, G., Gries, T., Roth, G., Schubnell, M., 2011. Structure, properties, and phase transitions of melt-spun poly(vinylidene fluoride) fibers. J. Appl. Polym. Sci. 120, 21–35. https://doi.org/10.1002/app.33087

Su, J., 2007. Ferroelectric Polymers for Electromechanical Functionality, in: Kim, K.J., Tadokoro, S. (Eds.), Electroactive Polymers for Robotic Applications: Artificial Muscles and Sensors. Springer London, London, pp. 91–120. https://doi.org/10.1007/978-1-84628-372-7_4

Suresh Kumar, K.S., 2009. Electric circuits and networks. Dorling Kindersley, New Delhi.

Takamatsu, S., Kobayashi, T., Shibayama, N., Miyake, K., Itoh, T., 2012. Fabric pressure sensor array fabricated with die-coating and weaving techniques. Sens. Actuators Phys. 184, 57–63. https://doi.org/10.1016/j.sna.2012.06.031

Takamatsu, S., Yamashita, T., Itoh, T., 2016. Meter-scale large-area capacitive pressure sensors with fabric with stripe electrodes of conductive polymer-coated fibers. Microsyst. Technol. 22, 451–457. https://doi.org/10.1007/s00542-015-2498-3

Takase, Y., Lee, J.W., Scheinbeim, J.I., Newman, B.A., 1991. High-temperature characteristics of nylon-11 and nylon-7 piezoelectrics. Macromolecules 24, 6644–6652. https://doi.org/10.1021/ma00025a014

Umeda, M., Nakamura, K., Ueha, S., 1997. Energy Storage Characteristics of a Piezo-Generator using Impact Induced Vibration. Jpn. J. Appl. Phys. 36, 3146. https://doi.org/10.1143/JJAP.36.3146

Vassiliadis, S.G., Matsouka, D., Potirakis, S., Siores, E., 2012. Measurements of the electrical properties of piezoelectric yarns. Presented at the V. International Technical Textiles Congress, Izmir, Turkey.

Vassiliadis, S.G., Matsouka, D., Vossou, C.G., Prekas, K., Potirakis, S., Soin, N., Siores, E., 2014. Measurement of the electrical power produced by piezoelectric fibres. Presented at the XIII International Izmir Textile and Apparel Symposium, Izmir, Turkey.

Vatansever, D., Hadimani, R.L., Shah, T., Siores, E., 2012a. Piezoelectric Mono-Filament Extrusion for Green Energy Applications from Textiles. J. Text. Eng. Tekst. Ve Mühendis 19, 1–5.

Vatansever, D., Hadimani, R.L., Shah, T., Siores, E., 2011. Characterisation of Energy Generating PolyVinylidene Fluoride (PVDF) Based Piezoelectric Filament. Adv. Mater. Res. 410, 366–369. https://doi.org/10.4028/www.scientific.net/AMR.410.366

Vatansever, D., Siores, E., Hadimani, R.L., Shah, T., 2011. Smart Woven Fabrics In Renewable Energy Generation. https://doi.org/10.5772/24790

Vatansever, D., Siores, E., Shah, T., 2012b. Alternative Resources for Renewable Energy: Piezoelectric and Photovoltaic Smart Structures, in: Singh, D.B.R. (Ed.), Global Warming - Impacts and Future Perspectives. InTech.

Vossou, C.G., Vassiliadis, S.G., Matsouka, D., Siores, E., 2013. Computational modelling of piezoelectric fibres. Presented at the The International Istanbul Textile Congress, Istanbul Turkey.

Walter, S., Steinmann, W., Gries, T., Seide, G., Schedukat, N., Roth, G., 2010. Melt-spun polyvinylidene-fluoride fibers of textile fineness. Chem. Fibers Int. 60, 49–51.

Walter, S., Steinmann, W., Schütte, J., Seide, G., Gries, T., Roth, G., Wierach, P., Sinapius, M., 2011. Characterisation of piezoelectric PVDF monofilaments. Mater. Technol. 26, 140–145. https://doi.org/10.1179/175355511X13007211258962

Walter, S., Steinmann, W., Seide, G., Gries, T., Roth, G., 2012. Development of innovative fibre materials for technical applications - Fine polyvinylidene fluoride filaments and fabrics. Filtration 12, 60–64.

Whatmore, R.W., 1991. Piezoelectric and Pyroelectric Materials and Their Applications. Electron. Mater. Silicon Org. 283.

Wijesiriwardana, R., Mitcham, K., Hurley, W., Dias, T., 2005. Capacitive fiber-meshed transducers for touch and proximity-sensing applications. IEEE Sens. J. 5, 989–994. https://doi.org/10.1109/JSEN.2005.844327

Williams, C.B., Yates, R.B., 1996. Analysis of a micro-electric generator for microsystems. Sens. Actuators Phys., Proceedings of the 8th International Conference on Solid-State Sensors and Actuators Eurosensors IX 52, 8–11. https://doi.org/10.1016/0924-4247(96)80118-X

Yang, C.M., Yang, T.L., Wu, C.C., Hung, S.H., Liao, M.H., Su, M.J., Hsieh, H.C., 2014. Textile-based capacitive sensor for a wireless wearable breath monitoring system, in: 2014 IEEE International Conference on Consumer Electronics (ICCE).

Presented at the 2014 IEEE International Conference on Consumer Electronics (ICCE), pp. 232–233. https://doi.org/10.1109/ICCE.2014.6775985

Yang, H., Lightner, C.R., Dong, L., 2012. Light-Emitting Coaxial Nanofibers. ACS Nano 6, 622–628. https://doi.org/10.1021/nn204055t

Yoon, H.-S., 2005. Modeling, Optimization, and Design of Efficient Initially Curved Piezoceramic Unimorphs for Energy Harvesting Applications. J. Intell. Mater. Syst. Struct. 16, 877–888. https://doi.org/10.1177/1045389X05055759